United States Court of Appeals

for the Second Circuit

APPENDIX

DEFERRED JOINT APPENDIX TO THE BRIEFS
Vol. 1 of 3
Pages 1 - 423

B
V/S

74-1683

74-1687

IN THE
UNITED STATES COURT OF APPEALS
FOR THE SECOND CIRCUIT

No. 74-1683

HOOKER CHEMICALS AND PLASTICS CORPORATION, STAUFFER CHEMICAL COMPANY, AND MONSANTO COMPANY,

Petitioner,

v.

RUSSELL E. TRAIN,

Respondent.

No. 74-1687

HOOKER CHEMICALS AND PLASTICS CORPORATION, STAUFFER CHEMICAL COMPANY, AND MONSANTO COMPANY,

Petitioner,

v.

RUSSELL E. TRAIN,

Respondent.

UNITED STATES ... DEC 3

On Petition For Review Of Action Of The
Administrator Of The Environmental Protection Agency

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December 20, 1974

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PREFACE

On September 20, 1974, this Court granted the Stipulation and Motion of the parties for leave to file a single deferred appendix in Hooker Chemicals and Plastics Corp., et al. v. Russell E. Train, No. 74-1683 and Hooker Chemicals and Plastics Corp., et al. v. Russell E. Train, No. 74-1687 and to consider the certified index of the record as the record in these cases.

The pagination of this Deferred Joint Appendix reflects the serial pagination of the entire administrative record certified to the Court by the Environmental Protection Agency (EPA), through EPA's Certified Index To The Record dated June 26, 1974. Of the 1,800 pages in the entire record as certified, approximately 850 pages have been reproduced in this Appendix. Consequently, the pages of this Appendix are not consecutively paginated throughout, but rather reflect the intentional omission of approximately 950 pages.

The Table of Contents of this Deferred Joint Appendix is comprised of the Certified Index of Record originally filed by EPA. Thus, for the convenience of the Court, the Table of Contents reflects the entire record and not merely the pages of the record reproduced in this Appendix.

IN THE UNITED STATES COURT OF APPEALS

FOR THE SECOND CIRCUIT

NO. 74-1687

HOOKER CHEMICALS & PLASTICS CORPORATION, et al., Petitioners

v.

RUSSELL E. TRAIN, Respondent

NO. 74-1683

HOOKER CHEMICALS & PLASTICS CORPORATION, et al., Petitioners

v.

RUSSELL E. TRAIN, Respondent

CERTIFIED INDEX TO THE RECORD

The Environmental Protection Agency hereby certifies that the material indexed and described below constitutes the complete record in the rulemaking proceedings before the Agency which resulted in the issuance of the regulations complained of in the above petitions for review.

By the Environmental Protection Agency

In witness whereof I have hereunto subscribed my name this 26th day of June, 1974 at Washington, D.C.

Charles H. Elkins

Acting Assistant Administrator for
Water and Hazardous Materials

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9. Economic Analysis of Proposed Effluent Guidelines - The Industrial Phosphate Industry, U. S. Environmental Protection Agency (August 1973) 1184-1244

10. Comments on Proposed Regulations for the Phosphate Manufacturing Point Source Category published on September 7, 1973.

1. John P. Philbin, Mobil Oil Corporation, October 8, 1973 1245-1247

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DRAFT

DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS OF PERFORMANCE

NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

PREPARED BY GENERAL TECHNOLOGIES CORPORATION
FOR UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
UNDER CONTRACT NUMBER 68-01-1513

JUNE 1973

NOTICE

The attached document is a DRAFT CONTRACTOR'S REPORT. It includes technical information and recommendations submitted by the Contractor to the United States Environmental Protection Agency ("EPA") regarding the subject industry. It is being distributed for review and comment only. The report is not an official EPA publication and it has not been reviewed by the Agency.

The report, including the recommendations, will be undergoing extensive review by EPA, Federal and State agencies, public interest organizations and other interested groups and persons during the coming weeks. The report and in particular the contractor's recommended effluent limitations guidelines and standards of performance is subject to change in any and all respects.

The regulations to be published by EPA under Sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended, will be based to a large extent on the report and the comments received on it. However, pursuant to Sections 304(b) and 306 of the Act, EPA will also consider additional pertinent technical and economic information which is developed in the course of review of this report by the public and within EPA. EPA is currently performing an economic impact analysis regarding the subject industry, which will be taken into account as part of the review of the report. Upon completion of the review process, and prior to final promulgation of regulations, an EPA report will be issued setting forth EPA's conclusions concerning the subject industry, effluent limitations guidelines and standards of performance applicable to such industry. Judgements necessary to promulgation of regulations under Sections 304(b) and 306 of the Act, of course, remain the responsibility of EPA. Subject to these limitations, EPA is making this draft contractor's report available in order to encourage the widest possible participation of interested persons in the decision making process at the earliest possible time.

The report shall have standing in any EPA proceeding or court proceeding only to the extent that it represents the views of the Contractor who studied the subject industry and prepared the information and recommendations. It cannot be cited, referenced, or represented in any respect in any such proceedings as a statement of EPA's views regarding the subject industry.

U. S. Environmental Protection Agency
Office of Air and Water Programs
Effluent Guidelines Division
Washington, D. C. 20460

DRAFT

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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS OF PERFORMANCE

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DRAFT

ABSTRACT

A study was made of the non-fertilizer phosphorus chemicals industry by the General Technologies Corporation for the Environmental Protection Agency, for the purpose of developing effluent limitations guidelines, Federal standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act Amendments of 1972.

For the purpose of this study, the non-fertilizer phosphorus chemicals industry was defined as the manufacture of the following chemicals: phosphorus (and by-product ferrophosphorus), phosphoric acid (dry process only), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, phosphorus oxychloride, sodium tripolyphosphate and the calcium phosphates.

Effluent limitations guidelines were developed as a result of this study, defining the degree of effluent reduction attainable through the application of:

Level I, the best practicable control technology currently available, and

Level II, the best available technology economically achievable.

The Level I and Level II degrees of effluent reduction must by law be achieved by existing point sources by July 1, 1977 and by July 1, 1983 (respectively).

Level III, the standards of performance for new sources, was also defined; as were the pretreatment requirements with respect to minicipal treatment of the industry's wastewaters.

Except for PCl_3 and $POCl_3$ manufacture, the recommended Level I guideline for the entire industry was zero discharge of process water. The quantitative limitations upon each type of pollution parameter permitted for PCl_3 and $POCl_3$ manufacturing discharges were defined; they are basically the remaining constituents after wastewater neutralization and removal of suspended solids. No toxic materials may be discharged.

For Level II, application of the best available technologies for treating dissolved solids would enable the PCl_3 and $POCl_3$ manufacturing operations to achieve zero discharge. Upon judgement that this would be economically achievable, the recommendation was made that the Level II (and Level III) guideline be zero discharge of all process water from the entire industry.

The recommendation for non-contact cooling water discharges is that they be permitted for Levels I, II and III providing they meet specific conditions restricting their damage to the environment and providing for emergency procedures in the event of their contamination.

The recommendation for pretreatment standards specifically covers flowrate, total suspended solids, total dissolved solids, total phosphate, pH, heavy metals, and toxic materials.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the non-fertilizer phosphorus chemicals industry was divided into the phosphorus production segment, the phosphorus-consuming segment, and the phosphates segment.

The phosphorus production segment of the industry is characterized by large quantities of raw process wastes, including highly-toxic phossy water and highly-acidic scrubber and quenching wastewaters, both containing large quantities of fluorides, other dissolved solids, and suspended solids. Through a combination of in-process controls and end-of-process treatments, several plants within this segment have achieved zero discharge of phossy water, two have achieved zero discharge of other process wastewaters, and one has achieved zero discharge of any wastewater. While other plants now demonstrate abatement practices resulting in 97 per cent or greater reduction in the raw waste load before discharge, the total recycle of process water without and discharge has been aptly demonstrated using the best practicable control technology.

The phosphorus-consuming segment of the industry is characterized by the absence of direct process wastewater; the chemicals produced are readily hydrolyzed so that the processes are essentially dry. However, just because the products are readily hydrolyzed, water is universally used for air-pollution abatement scrubbing of tail gases, for periodic cleaning of reaction vessels, and for the general washing of shipping containers; all resulting in acidic wastewaters. In addition, water is used in protecting and transferring the raw material, elemental phosphorus, and phossy water is therefore a raw waste from this segment. Except for the manufacture of dry-process phosphoric acid (where in-process control has been demonstrated to achieve zero discharge of aqueous wastes), this segment has not yet achieved sufficient reduction of effluents. The application, however, of currently-available technology is shown by this study to permit total recycle of wastewaters (and so zero discharge) for the manufacture of P_2O_5 and P_2S_5; and to achieve the neutralization and

of process wastes and pollutants in raw gas[illegible]

NOTICE: THESE ARE TENTATIVE RECOMMENDATIONS BASED UPON INFORMATION IN THIS REPORT AND ARE SUBJECT TO CHANGE BASED UPON COMMENTS RECEIVED AND FURTHER INTERNAL REVIEW BY EPA.

removal of most suspended solids prior to discharge for the manufacture of PCl_3 and $POCl_3$. For these latter two processes, more expensive but still economically achievable technologies are available for treating the chlorides so as to achieve zero discharge.

The phosphates segment of the industry, i.e., the group of chemicals manufactured from phosphoric acid, is characterized by acids and by finely-divided solids in the raw aqueous wastes. Several plants have already achieved zero discharge by in-process controls and by end-of-process treatment; and this study shows how the entire segment may achieve ~~zero discharge~~ the end of by applying currently-available practicable technology.

The general conclusion reached is that the industry has already solved its most serious raw waste problem, that is, the abatement of water pollution from phosphorus-producing facilities; and that the very high-volume manufacturing processes (phosphorus, phosphoric acid, sodium tripolyphosphate, and feed-grade calcium phosphate) have already achieved ~~zero~~ discharge. The remainder of the industry, made up of much smaller-volume plants, has lagged behind in effluent reduction, but technology is available to make the entire industry exemplary.

of process waste water pollutants to navigable waters.

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Rewrite completely

SECTION II

RECOMMENDATIONS

discharge standard based on BPCTCA for the following

The recommended Level I guideline for process water is ~~zero~~ no discharge for the manufacture of the following chemicals:

std

- Phosphorus (and Ferrophosphorus)
- Phosphoric Acid (Dry Process)
- Phosphorus Pentoxide
- Phosphorus Pentasulfide
- Sodium Tripolyphosphate
- Calcium Phosphates (Food Grade)
- Calcium Phosphates (Animal Feed Grade)

The recommended ~~Level I guidelines~~ for process water from the manufacture of phosphorus trichloride and of phosphorus oxychloride are listed in Table 1.

The recommended Level II guideline for process water is zero discharge for the manufacture of the following chemicals:

- Phosphorus (and Ferrophosphorus)
- Phosphoric Acid (Dry Process)
- Phosphorus Pentoxide
- Phosphorus Pentasulfide
- Phosphorus Trichloride
- Phosphorus Oxychloride
- Sodium Tripolyphosphate
- Calcium Phosphates (Food Grade)
- Calcium Phosphates (Animal Feed Grade)

The recommended ~~Level III guideline~~ for process water is the same as the above ~~Level II guideline~~.

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Table 1. Recommended Level I Effluent Guidelines for the Manufacture of Phosphorus Trichloride and Phosphorus Oxychloride. (Process Water)

The recommended Level I guidelines for process water for the manufacture of PCl_3 and $POCl_3$ are:

		Phosphorus Trichloride	Phosphorus Oxychloride
Total Suspended Solids:	kg/kkg	0.7	0.15
	lbs/ton	1.4	0.3
Total Dissolved Solids:	kg/kkg	5	3.5
	lbs/ton	10	7
pH		6-10.5	6-10.5

The above guidelines apply to monthly average values. The maximum values for daily averages of total suspended solids and total dissolved solids are twice the monthly average values. The daily average pH limitation is the same as the monthly average limitation. Additional restrictions upon the discharges are:

1. Zero elemental phosphorus discharged.
2. Arsenic compounds permitted only at the naturally-occuring level in the discharged phosphorus compounds. Under no circumstances is the discharge of arsenic compounds permitted when they exist in an enriched state (i.e., as residues from the purification of phosphorus compounds).
3. No discharge of other heavy metals or of toxic materials is permitted.

The recommendations for cooling water and blowdown discharges are:

Level I

An allowed discharge of all non-contact cooling waters provided that the following conditions are met:

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(1) No toxic or hazardous pollutants are added. Cooling waters discharged must not have levels of chromate or other toxic pollutants higher than that of the intake water or receiving water, whichever is lower.
(2) Thermal pollution be in accordance with local water quality standards.
(3) No process waters be added to the cooling waters prior to discharge.
(4) All non-contact cooling waters should be monitored to detect leaks from the process and provisions should be made for emergency treatment prior to release.

An allowed discharge of water treatment, cooling tower and boiler blowdowns provided these do not contain toxic or otherwise hazardous materials such as chromium or cadmium and are within the required pH range of 6 to 9 as measured both as a daily average and a monthly average.

Levels II and III

The same as Level I except that monitoring shall be required for process leaks and provisions made for emergency holding facilities for cooling water contaminated by leaks until such time as they can be treated.

The recommended pretreatment standards are:
1. An impact analysis of the wastewater flowrate (including time-varying effects) upon the hydraulic capacity of the public treatment plant be provided by the phosphorus chemicals plant.
2. The maximum amounts of total dissolved solids be the same as the applicable Levels I, II, or III effluent limitation guidelines.
3. The pH must be between 6 and 10.5.
4. Zero contribution of heavy metals and toxic materials.
5. The maximum concentration of Total Suspended Solids be 250 mg/l.
6. The maximum concentration of total phosphate (as PO_4) be 30 mg/l.

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SECTION III

INTRODUCTION

1.0 PURPOSE AND AUTHORITY

The United States Environmental Protection Agency (EPA) is charged under the Federal Water Pollution Control Act Amendments of 1972 with establishing effluent limitations which must be achieved by point sources of discharge into the navigable water of the United States. The Act requires the achievement by July 1, 1977, of effluent limitations which require the application of the "best practicable control technology currently available", and by July 1, 1983, the achievement of effluent limitations which require the application of the "best available technology economically achievable".

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where praticable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The

regulations proposed herein set forth effluent limitation guidelines pursuant to Section 304(b) of the Act for the non-fertilizer phosphorus chemicals industry source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b)(1)(A) of the Act, to propose regulations establishing Federal Standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcements of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the non-fertilizer phosphorus chemicals industry source category, which was included within the list published January 16, 1973.

2.0 SUMMARY OF METHODS USED FOR DEVELOPMENT OF EFFLUENT LIMITATION GUIDELINES AND STANDARDS OF PERFORMANCE

The Environmental Protection Agency has determined that a rigorous approach including plant surveying and verification testing is necessary for the promulgation of effluent standards from industrial sources. A systematic approach to the achievement of the required guidelines and standards includes the following:

(a) Categorization of the industry and determination of those industrial categories for which separate effluent limitations and standards need to be set;

(b) Characterization of the waste loads resulting from discharge within industrial categories and subcategories;

(c) Identification of the range of control and treatment technology within each industrial category and subcategory;

(d) Identification of those plants having the best practical technology currently available (exemplary plants); and

(e) Generation of supporting verification data for the best practical technology including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable current technology.

This report describes the results obtained from application of the above approach to the non-fertilizer phosphorus chemicals industry, as defined

for the purposes of this study as the following list of products:

Elemental Phosphorus and Ferrophosphorus
Dry-Process Phosphoric Acid
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphorus Trichloride
Phosphorus Oxychloride
Sodium Tripolyphosphate
Calcium Phosphates (Non-Fertilizer)

The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner. The point source category was first subcategorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such subcategorization was based upon raw material used, product produced, manufacturing process employed, and other factors. The raw waste characteristics for each subcategory were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents (including thermal) of all waste waters including toxic constituents and other constituents which result in taste, odor, and color in water or aquatic organisms. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies, which are existent or capable of being designed for each subcategory. It also included an identification in terms of the amount of constituents (including thermal) and the chemical, physical, and biological characteristics of pollutants, of the effluent level resulting from the application of each of the treatment and control technology and the required implementation time were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation were also identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constituted the best practicable control

technology currently available, "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives". In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects, process changes, non-water quality environmental impact (including energy requirements), and other factors.

The data for identification and analyses were derived from a number of sources. These sources included EPA research information, published literature, previous EPA technical guidance for inorganic chemicals, alkali and chlorine industries, qualified technical consultation, and on-site visits and interviews at exemplary manufacturing plants throughout the United States. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are ~~included~~ listed in Section XIII of this document.

3.0 GENERAL DESCRIPTION OF THE INDUSTRY

The flow of materials in the non-fertilizer phosphorus chemicals industry is depicted in Figure 1. This industry is almost entirely based upon the production of elemental phosphorus from mined phosphate rock. The economics have dictated that the phosphorus production facilities be located at the sources of the raw material, which are in three areas in the United States: Tennessee, the Idaho-Montana area, and Florida. The key in plant siting decisions is the relative weights of phosphate rock, elemental phosphorus and phosphoric acid (about 10:1:4). Hence, the rock is processed close to the mine and the acid is produced close to its consumption point; the relatively low-weight elemental phosphorus is almost universally the form shipped from place to place.

Ferrophosphorus, widely used in the metallurgical industries, is a direct by-product of the phosphorus production process, since most furnace-grade phosphate rock contains 2 to 6 percent iron oxide.

Over 87 percent of the elemental phosphorus is used to manufacture high-grade phosphoric acid by the furnace or "dry" process (as opposed to the wet process which converts phosphate rock directly into phosphoric acid; this lower-grade wet process acid is almost exclusively used in the fertilizer industry and is separately discussed in another portion of this EPA effort). The remainder of the elemental phosphorus is either marketed directly or is converted to chemicals such as phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus

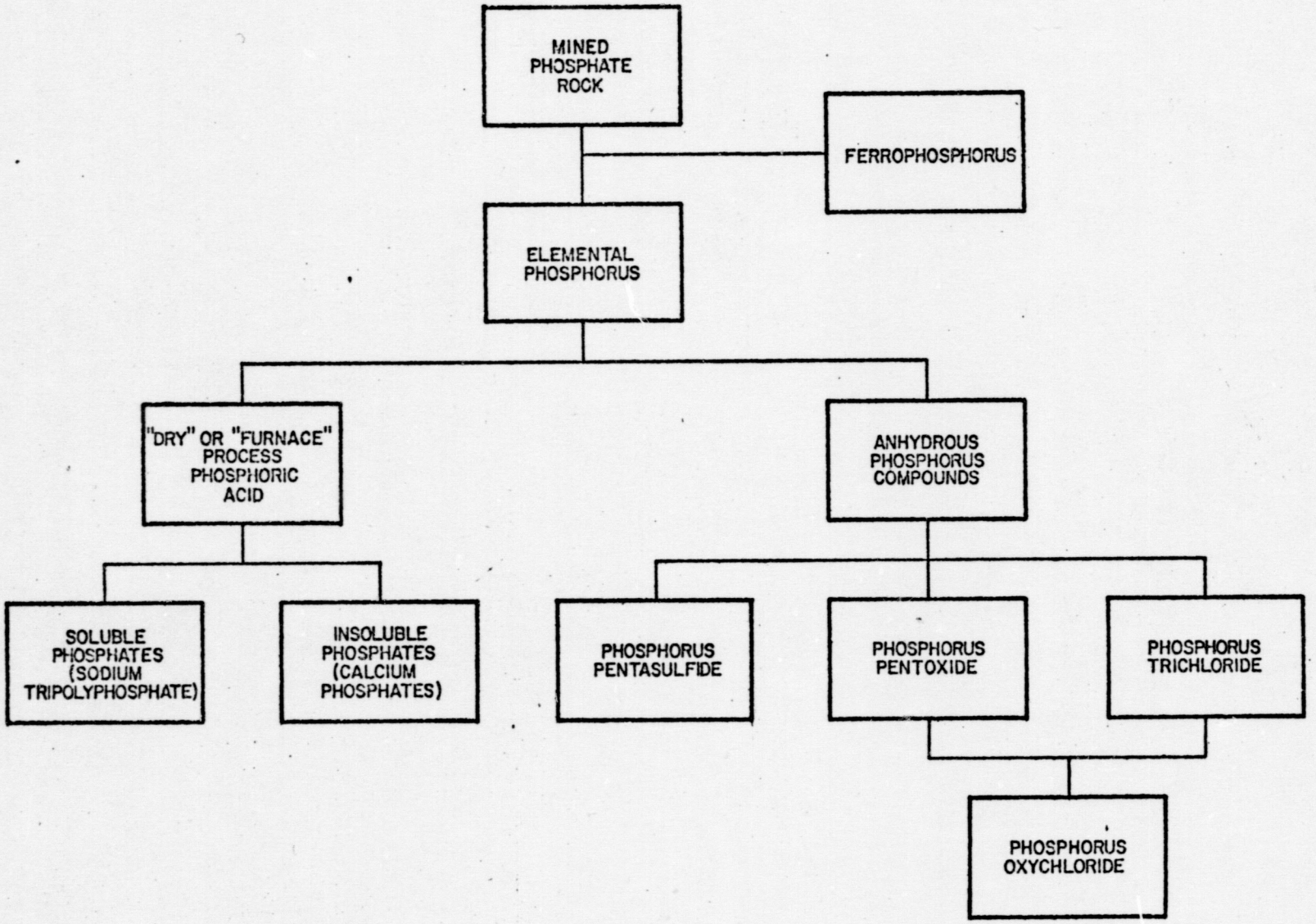

FIGURE 1

FLOW OF MATERIALS IN THE NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

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oxychloride. These latter chemicals are chiefly used in synthesis in the organic chemicals industry.

Much of the furnace-grade phosphoric acid is directly marketed, largely to the food industry and to the high-grade fertilizer industry. Phosphoric acid is also used to manufacture two basic classes of phosphates: water-soluble phosphates used in detergents and for water treatment, typified by sodium tripolyphosphate; and water-insoluble phosphates which are used in animal feeds and in foods, typified by the calcium phosphates.

Table 2 lists production tonnages for these chemicals as reported by the U. S. Bureau of Census. ~~(1)~~

The processes involved in the non-fertilizer phosphorus chemicals industry are very briefly as follows:

Elemental phosphorus and ferrophosphorus are manufactured by the reduction of phosphate rock by coke in very large electric furnaces, using silica as a flux. Very large quantities of water are circulated for cooling the very hot equipment, for cooling and granulating the slag, and for condensing the phosphorus vapor from the furnace. Since water is both non-reactive and immiscible with liquid phosphorus, water is used extensively in direct contact with phosphorus for heat transfer, for materials transfer, for protection from the atmosphere, and for purification. This study is concerned with manufacturing operations subsequent to receiving wooled phosphate rods at the phosphorus production facility. Ore benefication is commonly but not exclusively conducted at a separate off-site location. The huge waste load from benefication, 7500 Kg of gangue per Kg of phosphorus eventually produced, warrants a separate study as a segment of the mining industry.

Phosphoric acid manufactured by the "dry" or furnace process consists of the burning of liquid phosphorus in air, the subsequent quenching and hydrolysis of the P_2O_5 vapor, and the collection of the phosphoric acid mists. The operation uses cooling water and process water is consumed in making the aqueous acid. Solid wastes may be generated should a plant perform subsequent purification of the acid.

The manufacture of the anhydrous phosphorus chemicals (P_2O_5, P_2S_5, and PCl_3) is essentially by the direct union of phosphorus with the corresponding element. Phosphorus oxychloride, $POCl_3$, is manufactured from PCl_3 and air or from PCl_3, P_2O_5, and chlorine. Water use is limited to cooling water, to water for transferring elemental phosphorus, to scrubber water, and to wash water for reaction vessels and shipping containers.

TABLE 2. U. S. Production of Non-Fertilizer Phosphorus Chemicals(1)

Chemicals	~~Metric Tons~~ kkg	~~Short~~ Tons	Number of Plants
Phosphorus	495,000	545,000	10
Ferrophosphorus	110,000*	121,000*	
Phosphoric Acid (Furnace Process)	1,640,000**	1,810,000**	25
Phosphorus Pentoxide	(withheld)	(withheld)	(withheld)
Phosphorus Pentasulfide	54,000	59,000	5
Phosphorus Trichloride	50,000	55,000	4
Phosphorus Oxychloride	28,000	31,000	4
Sodium Tripolyphosphate	945,000	1,040,000	17
Calcium Phosphates	536,000	592,000	7

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* Independently estimated.(2)

** Estimated as 87 percent of Phosphorus Consumption,(3) using 90 percent conversion, and stated as acid of 54 percent P_2O_5. The total production of phosphoric acid, both wet and dry was 5,650,000 kkg (6,240,000 short tons).

Sodium tripolyphosphate is manufactured by the neutralization of phosphoric acid with the appropriate proportion of caustic soda and soda ash in mix tanks. The resulting mixture of mono- and di-sodium phosphates is dried and the crystals calcined to produce the tripolyphosphate.

The calcium phosphates are similarly made by the neutralization of phosphoric acid with lime. The amount and type of lime used and the amount of water in the process determines whether anhydrous monocalcium phosphate, monocalcium phosphate monohydrate, dicalcium phosphate dihydrate, or tricalcium phosphate is the final product.

SECTION IV

INDUSTRY CATEGORIZATION

1.0 SEGMENTS OF THE INDUSTRY

For the purpose of waste treatment and effluent limitations, the non-fertilizer phosphorus chemicals industry may be divided into three discrete segments, which coincide with a breakdown of the industry according to the flow of materials as outlined in Section III.

1.1 The Phosphorus Production Segment

Phosphorus (and by-product ferrophosphorus) production stands by itself as a smelting operation, as opposed to more conventional chemical processes. In phosphorus production, a grossly impure raw material is involved, and raw wastes and by-products are generated which dwarf the quantities of the primary product. The remainder of the industry starts with relatively pure materials, waste streams are consequently much smaller.

1.2 The Phosphorus Consuming Segment

The chemicals that are made directly from elemental phosphorus (phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide and phosphorus trichloride) may also be grouped because aqueous wastes arise primarily from sources other than the direct process stream. Air pollution abatement unit operations, product purification residues, tail-gas seals, vessel cleanings, and leaks and spills are the sources of the aqueous waste streams. To this segment, phosphorus oxychloride has been added despite the fact that phosphorus is not a direct raw material of its production; however, the waste streams have similar origins.

1.3 The Phosphate Segment

The chemicals that are made from phosphoric acid (sodium tripolyphosphate and the calcium phosphates) constitute a separate segment because excess process water is used in their manufacture, and also because they are finely-divided solid products. The former characteristic gives rise to some aqueous wastes of direct process origin; the latter characteristic gives rise to aqueous wastes from wet dust scrubbing equipment.

2.0 PROCESS DESCRIPTIONS

Following is a description of each process in this industry. Process flow diagrams are included. In generating the following process descriptions, more-than-usual emphasis has been placed upon process features which generate aqueous wastes. The details of the waste stream character, however, has been left for discussion in Section V; the purpose of Section IV (in addition to providing a general understanding of the industry) is to identify the sources of aqueous wastes.

Much of the process data in this section was acquired by discussions with industry personnel and by observations of existing facilities. A large body of data also exists in the published literature, and was used extensively in the following discussion. Of particular usefulness were the publications of Beveridge and Hill,(4) of Barber,(5,6) Barber and Farr,(7) and LeMay and Metcalf(8) of The Tennessee Valley Authority, which supplied very specific operating details of TVA's facilities; of Ellwood,(9) and of Bryant, Holloway and Silber(10) of the Mobil Chemical Company. Standard reference books such as Faith, Keyes and Clark,(11) Kirk and Othmer,(12) and Shreve,(13) were also useful.

2.1 The Phosphorus Production Segment

Phosphorus is manufactured by the reduction of mined phosphate rock by coke in an electric furnace, with silica used as a flux. Slag, ferrophosphorus (from iron in the phosphate rock) and carbon monoxide are reaction by-products. The simplified overall reaction may be written:

$$2\,Ca_3(PO_4)_2 + 10\,C + 6\,SiO_2 \xrightarrow{1250 - 1500°C} P_4 + 10\,CO + 6\,CaSiO_3 \quad .$$

A typical material balance for the process is:

Raw Materials	kkg	ton	Products	kkg	ton
Phosphate Rock	10.0		Phosphorus	1.0	
Silica	1.5		Ferrophosphorus	0.3	
Coke	1.5		Slag	8.9	
			Carbon Monoxide	2.8	
Total	13.0 kkg		Total	13.0 kkg	

The electrical power consumption is approximately 15,400 KWH/kkg (14,000 KWH/ton) of phosphorus produced; part of this supplies the endothermic heat of reaction of 6,200 KWH/kkg of P_4.

The standard process, as pictured in Figure 2, consists of three basic parts: phosphate rock preparation, smelting in the electric furnace, and recovery of phosphorus.

a). Phosphate Rock Preparation. Phosphate rock ores are first blended so that the furnace feed is of uniform composition. The silica composition is important since the overall furnace feed must have a SiO_2/CaO ratio close to the eutectic composition for desired slag flow properties. The blended phosphate rock is carefully pretreated by drying, by agglomerating the particles, and by heat treating.

After the raw phosphate rock is dried, sizing or agglomeration is accomplished by pelletizing, briquetting, flaking, or "nodulizing", and pre-formed agglomerates are then calcined in a rotary kiln. The nodulizing operation performs simultaneous agglomeration and calcining by heating the rock to its incipient fusion point, with subsequent crushing, sizing, and recycling of fines. Sizing promotes the even distribution of gas flow within the furnace and results in more efficient heat transfer and lower total energy costs. The size of furnaces has dramatically increased in recent years, accentuating the needs for stoichiometric balance and thermal homogeneity within the charge (or "burden"). Heat treatment or calcining of the feed increases the strength and hardness of the particles, preventing large quantities of fines from being formed by attrition.

The calcining, at 1000 to 1400°C, also liberates water of hydration, organics, carbon dioxide, and fluorine at a much lower energy cost than would be required in the subsequent electric furnace operation. Since 25 percent of the manufacturing costs of phosphorus are for electric power, considerable effort is made to conserve this power. Moreover, by-product carbon monoxide from the smelting operation is available as a source of auxiliary energy.

The sizing and calcining operations are sources of dust and of fluorine fumes. The dust may be electrostatically precipitated, and the gases are scrubbed with water, removing fluorine as HF and H_2SiF_6. The dry dusts collected are normally recycled to the nodulizing operation.

b). Electric Furnace Operations. The burden of treated phosphate rock, coke, and sand is charged to the furnace by incrementally adding weighed quantities of each of the three materials to a common belt conveyor.

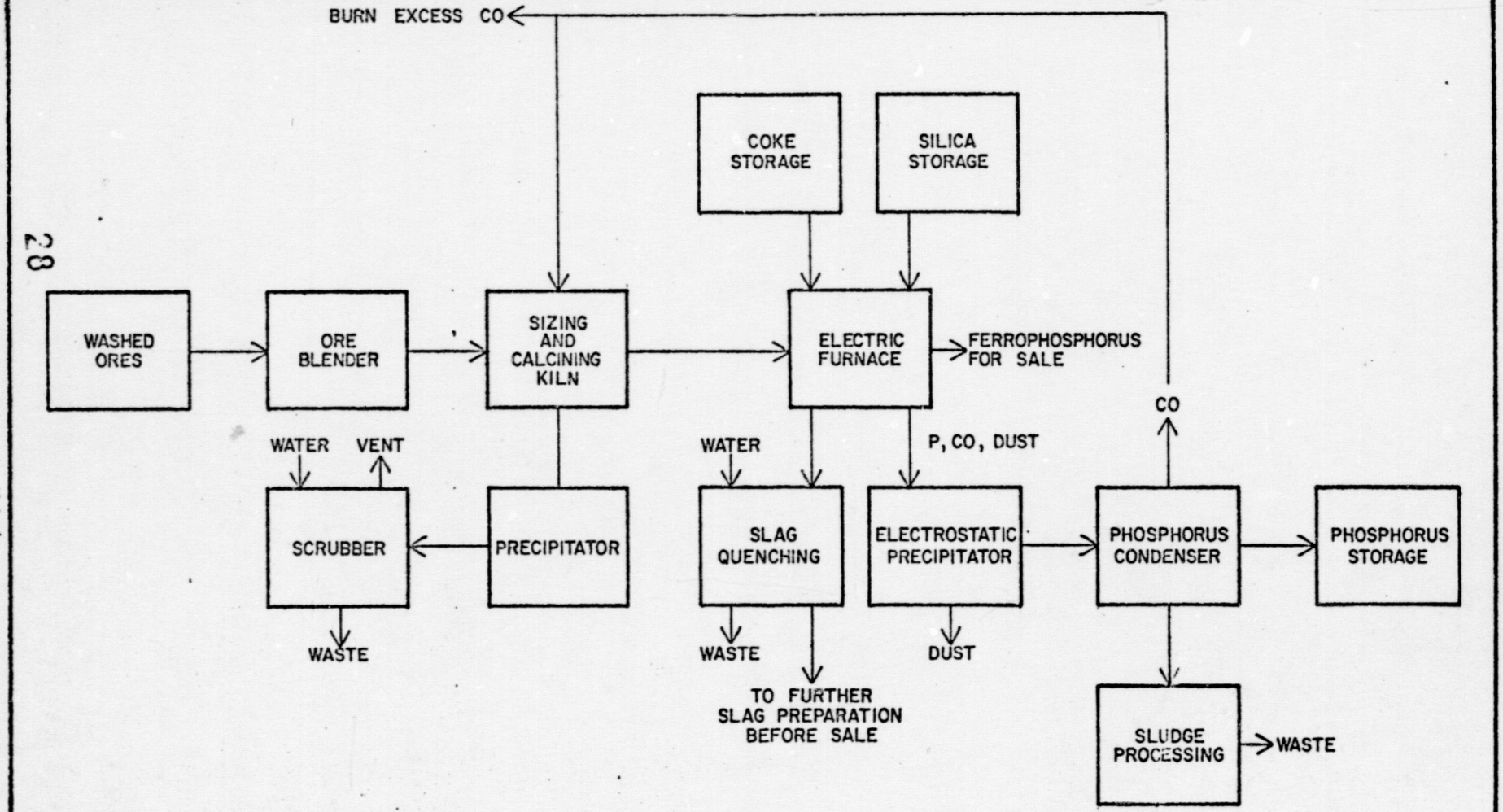

FIGURE 2
STANDARD PHOSPHORUS PROCESS FLOW DIAGRAM

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The furnace itself has a carbon crucible and carbon-lined steel sidewalls, with a two-foot-thick self-supporting cast concrete roof. In an effort to eliminate periodic roof replacement due to excessive cracking of the concrete, some newer furnaces have anti-magnetic (to avoid induction heating) stainless steel roof structures. Penetrations in the furnace are for feed chutes, for carbon electrodes, for tap holes for slag (upper liquid layer) and for ferrophosphorus (lower liquid layer), and for exhaust gases.

need sketch of furnace for clarity

Electric furnaces for phosphorus production have been dramatically increasing in size to achieve operating economies:

Year	Size of Largest Furnace in Operation		
	Megawatts	kkg/Year	Tons/Year
1950	25	13,600	15,000
1960	50	27,200	30,000
1970	65	36,300	40,000

An appreciation of the physical size may be attained from the fact that the largest carbon electrodes used are 1.5 to 1.8 meters (5 to 6 feet) in diameter and carry 50,000 amps each.

The furnace is extensively water-cooled. Cooling water is used for the electrical transformer, for the furnace shell, for the crucible bottom, for the fume hood, for the tapholes, and for the electrode joints. Newer furnaces use telescoping water seals on furnace electrodes; and for TVA-type furnaces with rotating crucibles, a water seal is provided between the crucible and the stationary roof.

The 2 to 6 percent Fe_2O_3 in the furnace-grade phosphate rock is reduced, with the iron recovered as the ferrophosphorus alloy:

$$Fe_2O_3 + 3C \rightarrow 2\ Fe + 3\ CO$$

$$8Fe + P_4 \rightarrow 4\ Fe_2P$$

The ferrophosphorus typically contains 59 percent iron and 22 percent phosphorus and is marketed for the production of phosphorus alloys. The vanadium content of ferrophosphorus adds to its value. Should the marketplace be favorable for ferrophosphorus, iron slugs can be added

to the furnace charge. Alternately, should a soft market for ferrophosphorus occur, the ferrophosphorus can be converted into high-grade metallurgical iron and fertilizer phosphates. An important degree of freedom is in the ore blending operation, where ores of appropriate iron content may be selected depending upon the ferrophosphorus market.

Slag and ferrophosphorus are tapped periodically. The air-cooled ferrophosphorus is sold in lumps to the metallurgical industry; no water is involved either in ferrophosphorus cooling or in subsequent product preparation.

The slag may typically contain 38 percent SiO_2 and 48 percent CaO, and also contain considerable quantities (depending of course upon the ore composition) of Al_2O_3, CaF_2, K_2O, and MgO, with traces of uranium and other heavy metals. The slag may be air-cooled, but water quenching is more typical. High-density slag is produced by adding water to molten slag in a pit, and by subsequently breaking it up and shipping aggregate for railroad bed or roadbed construction. Alternately, a high-velocity water stream may be used upon the molten slag to produce a low-density expanded or granulated slag, which has a market in concrete formulation. In either event, some of the fluorides from the slag are captured by the quenching water, either as soluble fluorides or as suspended solids.

There are numerous sources of fumes from the furnace operation. The feeding operation is a source of dust, and fumes are emitted from the electrode penetrations and from the tapping operations. These fumes, consisting of dust, phosphorus vapor (which is immediately oxidized to phosphorus pentoxide), and carbon monoxide are often collected and scrubbed.

c). Phosphorus Recovery. The hot furnace gases consisting of 90 percent CO and 10 percent P_4, pass through an electrostatic precipitator to remove the dust prior to phosphorus condensation. Unless this dust were removed, it would later be emulsified by liquid phosphorus and water, forming large amounts of "phosphorus mud" or sludge which would be difficult and costly to handle.

The precipitator is a most unusual piece of equipment. In the phosphorus process, the precipitator is in the main process stream, as opposed to its usual application in an exhaust stream. Because of this, it is gas-tight (especially since any air would cause phosphorus combustion). It operates at very high temperatures with the inlet gas approaching 540°C (1000°F), and its surfaces must be maintained hot to prevent phosphorus condensation (the dew point of phosphorus is 180°C (356°F)). The precipitator is typically a tube bundle, with the gas passing through

the tubes, and with a high-voltage wire along the axis of each tube. Both the wire and the tube are mechanically shaken to release the dust into a hopper. In some installations, the dust is a waste material sold as fertilizer; in others, the dust is slurried in water, pumped to a settling pond, and the solids are recycled to the raw feed for recovery of phosphates values (the clarified pond effluent is reused in the slurrying operation).

The high-voltage wires may be insulated from the shell with an oil seal; contaminated oil is periodically replaced with fresh oil. Alternately, a quartz seal may be used. The entire unit is heated either electrically or by an inert gas jacket of by-product carbon monoxide combustion gases.

Downstream of the precipitator, the phosphorus is condensed by direct impingement of a hot water spray, which is sometimes augmented by heat-transfer through water-cooled condenser walls. The liquid phosphorus (freezing point 44°C (111°F)) drains into a water sump, where the water maintains a seal from the atmosphere. This water is partially neutralized by addition of ammonia or caustic to minimize corrosion, and then is recirculated from the sump to the phosphorus condenser.

Liquid phosphorus is stored in steam-heated tanks under a water blanket and is transferred into tank cars by pumping or by hot water displacement. The tank cars also have a protective blanket of water and are equipped with steam coils for remelting at the destination.

Despite very high precipitator removal efficiencies, enough dust reaches the condensers to form some phosphorus mud, which is typically 10 percent dust, 30 percent water, and 60 percent phosphorus.

The condenser exhaust gases are mainly carbon monoxide, which is either burned in a flare or utilized for heating elsewhere in the plant.

~~2.2~~ The Phosphorus Consuming Segment

~~2.2.1~~ Phosphoric Acid (Dry Process)

Phosphoric acid is made from elemental phosphorus in the "dry" process, as opposed to the acidulation of phosphate rock in the "wet" process. The wet process is discussed in a separate report, dealing with the fertilizer industry, in this overall EPA effort. Furnace acid, as dry-process phosphoric acid is called, is relatively pure compared to wet-process acid, as Table 3 indicates. Consequently, the furnace acid is primarily used for preparing foodstuffs, detergents, and other high-

TABLE 3

Impurities in Phosphoric Acid (54% P_2O_5)

~~Source: Beveridge and Hill~~[4]

	Wet Process Acid	Furnace Acid
F, wt %	0.6 - 1.0	0.007
SO_3, wt %	2.7	0.003
Al_2O_3, wt %	0.9	0.001
Fe_2O_3, wt %	1.2	0.0007
Water insolubles, wt %	0.8	
Total Impurities, wt %	6.2 - 6.6	0.012
Density, Kg/l (lb/gal) @ 27°C (80°F)	1.72 (14.3)	1.57 (13.1)
Viscosity, cp @ 27°C (80°F)	85	18
Color	Black	Colorless

grade products; while wet acid is primarily used for preparing fertilizers and animal feed supplements.

In the standard dry process illustrated in Figure 3, liquid phosphorus is burned in air, the resulting gaseous phosphorus pentoxide is absorbed and hydrated in a spray of water, and the mist is collected with an electrostatic precipitator.

The standard reaction may be written:

$$P_4 + 5O_2 \rightarrow 2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4$$

Liquid phosphorus is stored under water in tanks heated with steam coils (the freezing point of phosphorus is 44°C (111°F)). The phosphorus may be fed to the burner by hot-water displacement in a feed tank, in a loop with a steam-heated displacement water tank and water pump. Alternately, the liquid phosphorus may be pumped directly.

There are variations in the design of the liquid phosphorus injector. Some producers achieve fine atomization using air in a dual-fluid injector (where the injection orifice can be large enough to prevent plugging). To prevent freezing of the phosphorus in upstream portions of the injector and yet to keep the injector tip cool, intricate use of both steam and cooling water has been simultaneously applied. Other designs have proven successful for phosphorus atomization, including the exploitation of extreme turbulence in a pre-combustion zone. Some form of temperature control is required, since red phosphorus formed at combustion temperatures much higher than 1650°C (3000°F) would color the resulting acid and would plug injector orifices.

In the combustion chamber, corrosion by P_2O_5 vapors and by hot phosphoric acid (formed from the moisture in the air) is countered by using a graphite lining. The steel shell of the combustion chamber is cooled by running water down its exterior surfaces. This mode of heat transfer is standard, pressurized cooling water is avoided since any leaks would result in premature hydration. Recent plants have been constructed with stainless steel combustion chambers.

The gas exiting from the combustion chamber is typically 540°C (1000°F), and is then hydrated with direct water sprays, which also reduces the temperature to 120°C (250°F) or less.

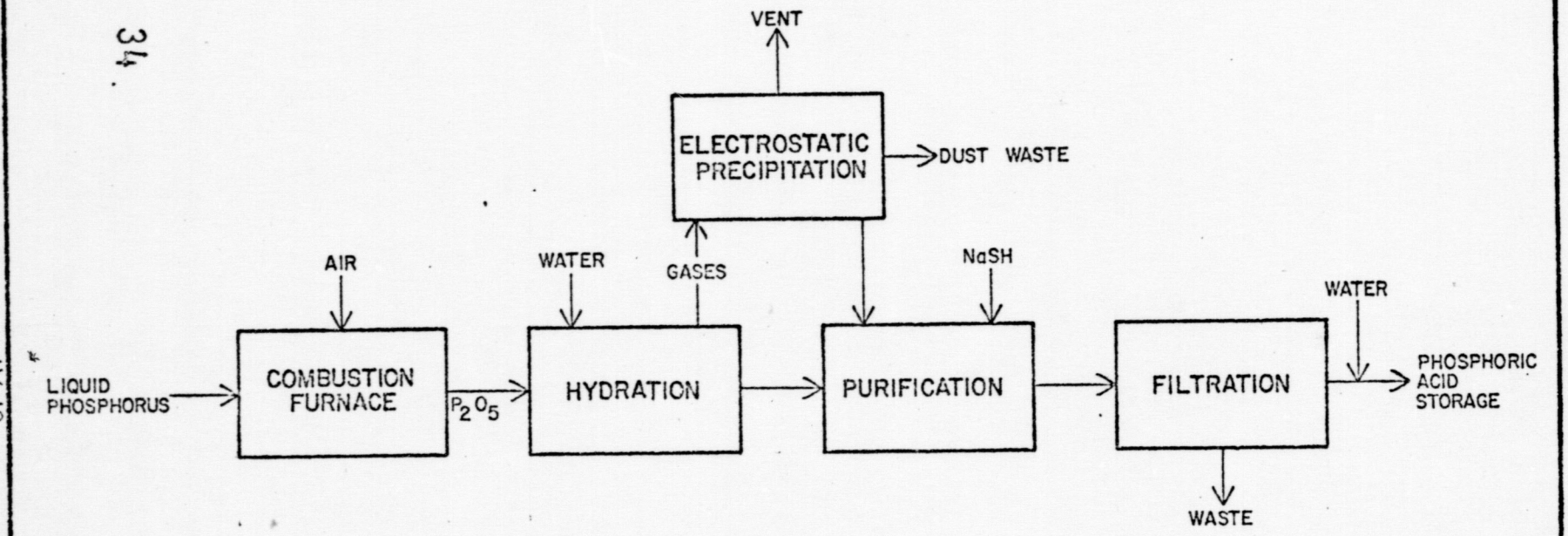

FIGURE 3
STANDARD PHOSPHORIC ACID FLOW DIAGRAM (DRY PROCESS)

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A variation of the standard process, illustrated in Figure 4, uses dilute acid for hydration instead of water. In this case, the make-up water is added in the vapor-liquid separation step. The rationale is that P_2O_5 vapor is absorbed more easily as the concentration of absorbing acid is increased. Another deviation from the standard process, also shown in Figure 4, is the use of a high pressure-drop venturi scrubber to complete the somewhat difficult hydration, and a screen-type demister and separation tower instead of an electrostatic precipitator to free the tail gases of the persistent acid mist.

When an electrostatic precipitator is used for collection of the phosphoric acid mist, the corrosivity requires the use of carbon tubes and stainless steel high-voltage wires. Those plants using a high pressure-drop venturi scrubber and a screen-type demister with a separation tower utilize stainless steel construction. Where dilute phosphoric acid is used in the hydrator, the make-up water is added in the separation tower. Regardless of process variation, phosphoric acid is made with a consumption of water; no aqueous waste streams are generated by the process.

The product acid is quite pure, but for the manufacture of food-grade acid, traces of arsenic must be removed. Arsenic occurs naturally with phosphorus in the ore (they are both Group V-A elements) at a level of about 0.075 kg of arsenic per kkg of phosphorus (0.15 lbs/ton).[14] The arsenic is quantitatively carried through into the acid, and is commonly removed by treatment with a soluble sulfide followed by filtration of the insoluble arsenic sulfide.

2.2.2 Phosphorus Pentoxide

The manufacture of solid anhydrous phosphorus pentoxide is similar to the first stages of phosphoric acid manufacture. Liquid phosphorus is burned in an excess of air:

$$P_{4(l)} + 5O_2 \rightarrow 2P_2O_{5(s)}$$

Figure 5 is a flow diagram for a standard phosphorus pentoxide manufacturing facility. A significant difference between the two processes is that in the anhydrous phosphorus pentoxide process, the air is dried to an extremely low dew point, since any moisture results in a lumpy and agglomerated product not suited for its uses as a reactive drying agent and as a reactive condensing agent in organic synthesis. Typically,

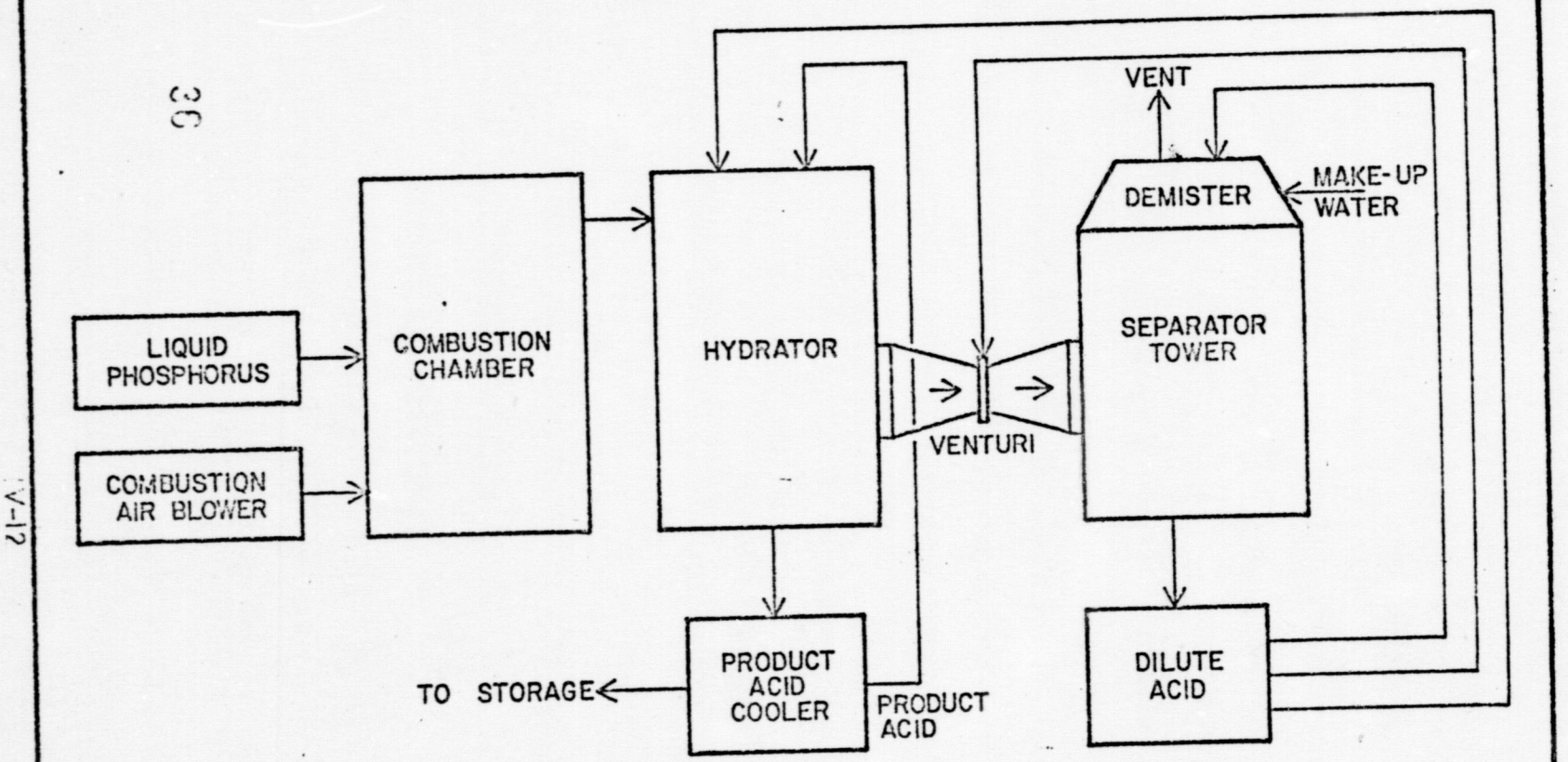

FIGURE 4
VARIATIONS OF PHOSPHORIC ACID (DRY) PROCESS

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FIGURE 5
PHOSPHORUS PENTOXIDE MANUFACTURE FLOW DIAGRAM

the ambient air is filtered, then refrigerated to achieve a dew point of -18 to -7°C (0 to 20°F), and then dried to a dew point of -46°C (-50°F) with silica gel.

After reaction of liquid phosphorus with excess dried air in the combustion chamber, the P_2O_5 vapor is condensed to a solid in a "barn", which is a room-like structure. Some installations utilize a more conventional tower for condensation. Both the combustion chamber and the barn (or tower) are cooled by an external flow of water down the surfaces; pressurized cooling water is avoided since any leaks would result in lumpy, unacceptable product.

Condensed phosphorus pentoxide solid is mechanically scraped from the walls using moving chains, and is discharged from the bottom of the barn or tower with a screw-type conveyor. The gases are vented to the atmosphere through a tail-gas water seal which absorbs any P_2O_5 vapor or solid carry-over. There is usually continuous water addition and overflow for the tail gas seal.

The product particle size is sensitive to the rate of cooling and condensation in the barn or tower. In a barn, the external surface-to-volume ratio is small, a relatively high temperature is maintained in the condensing unit, and rather large crystals may grow. In a tower, heat transfer is more rapid, and the product is very finely divided. One installation uses two towers in series; the first has much higher heat transfer rates and results in a coarser product than the second, and the products from the two towers are separately packaged.

2.2.3 Phosphorus Pentasulfide

The standard process for the manufacture of phosphorus pentasulfide, shown in Figure 6, is by direct union of the elements, both in liquid form:

$$P_{4(l)} + 10S_{(l)} \rightarrow 2P_2S_{5(l)}$$

The largest use of phosphorus pentasulfide is for the manufacture of lubricating oil additives.

Liquid sulfur (melting point 113°C (230°F)) is transferred from a steam-heated storage tank using submerged pumps, and liquid phosphorus (melting point 44°C (111°F)) is transferred by hot-water displacement. The highly exothermic reaction is usually carried out as a batch operation in stirred cast-iron pots. A "heel" of molten P_2S_5 (melting point 282°C (540°F)) from the previous batch is used to absorb the initial heat of

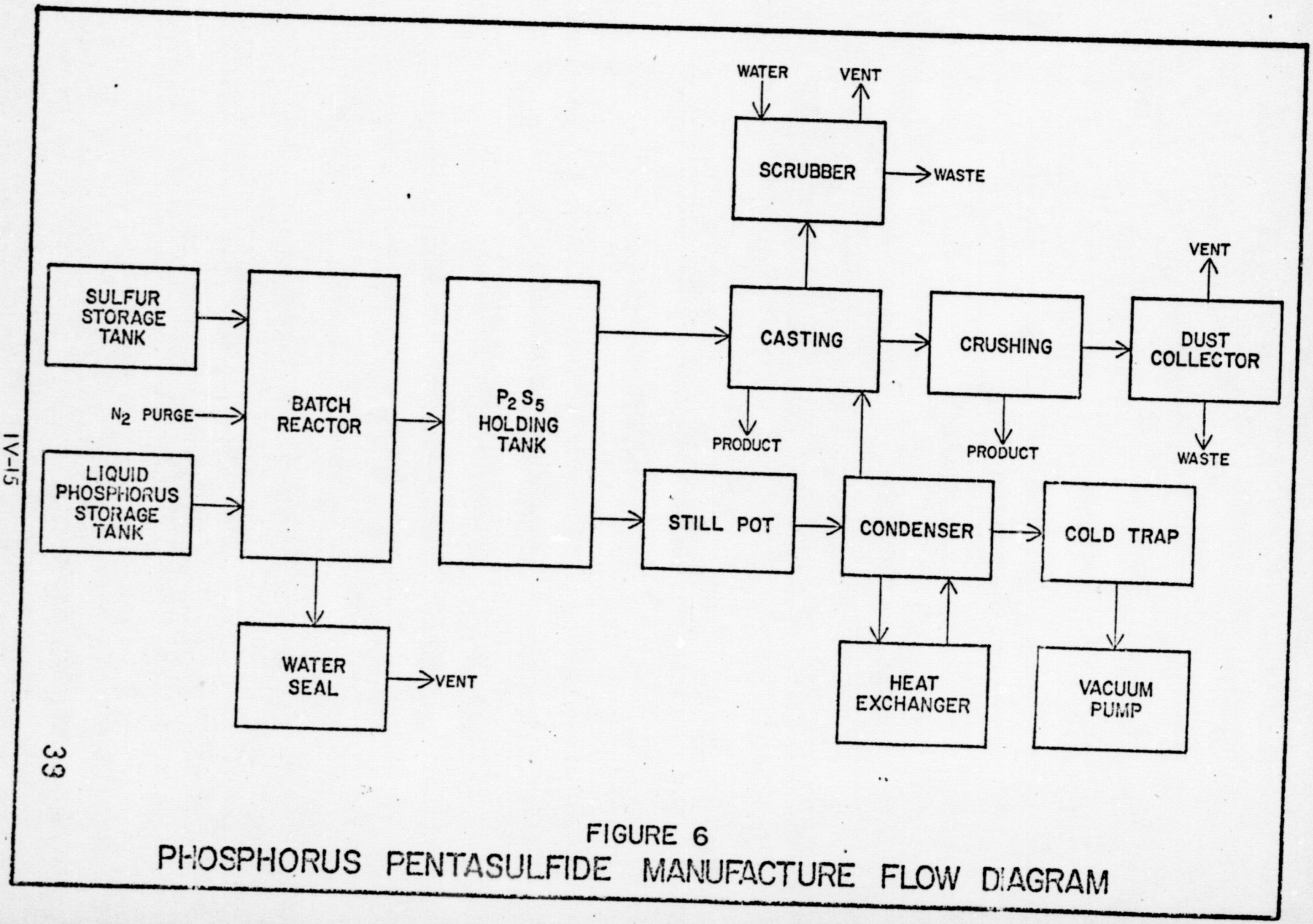

FIGURE 6
PHOSPHORUS PENTASULFIDE MANUFACTURE FLOW DIAGRAM

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reaction. Liquid phosphorus and liquid sulfur are incrementally added. Since the reactants and the product are extremely flammable at the reaction temperature, the reactor is continuously purged with nitrogen. A water seal is used in the vent line.

The batches from multiple reactors are forced into an electrically-heated (300°C (570°F)) P_2S_5 holding tank by nitrogen pressure. Some of the P_2S_5 is converted directly into product, while the rest is purified. Liquid P_2S_5 from the holding tank that is to be sold is cast directly into drums or into cones. When the molten product contacts air during casting, it ignites and fumes of P_2O_5 and SO_2 are generated. A fume hood and water scrubber are used. The cones, after cooling, are crushed and packaged; solid P_2S_5 does not auto-ignite in air. The dust from the crushing operation is removed in a dry separation system such as a cyclone.

The liquid P_2S_5 that is to be purified may be vacuum distilled (normal boiling point is 515°C (960°F)) in a continuous system. The condenser is cooled by a high-temperature heat transfer fluid, which in turn is cooled in a water-cooled heat exchanger. The condenser is operated between the melting and boiling points of the product. Molten purified P_2S_5 is then cast and crushed, sharing the fume scrubber and dust collection systems with the impure product operation.

An alternate mode of purification is the washing of crushed P_2S_5 with carbon disulfide, in which by-product phosphorus sesquisulfide (P_4S_3) and free sulfur are soluble.

~~2.2.4~~ Phosphorus Trichloride

Phosphorus trichloride, used extensively in organic synthesis, is manufactured directly from the elements:

$$P_{4(\ell)} + 6\ Cl_{2(g)} \rightarrow 4PCl_{3(\ell)}$$

The standard process is shown in Figure 7. Liquid phosphorus is charged to a jacketed batch reactor. Chlorine is bubbled through the charge, and phosphorus trichloride product (melting point -112°C (-173°F), boiling point 74°C (165°F)) is refluxed until all of the phosphorus is consumed. Some cooling water is used in the reactor jacket since the formation of PCl_3 is exothermic. Care is taken to avoid an excess of chlorine; otherwise, phosphorus pentachloride is formed.

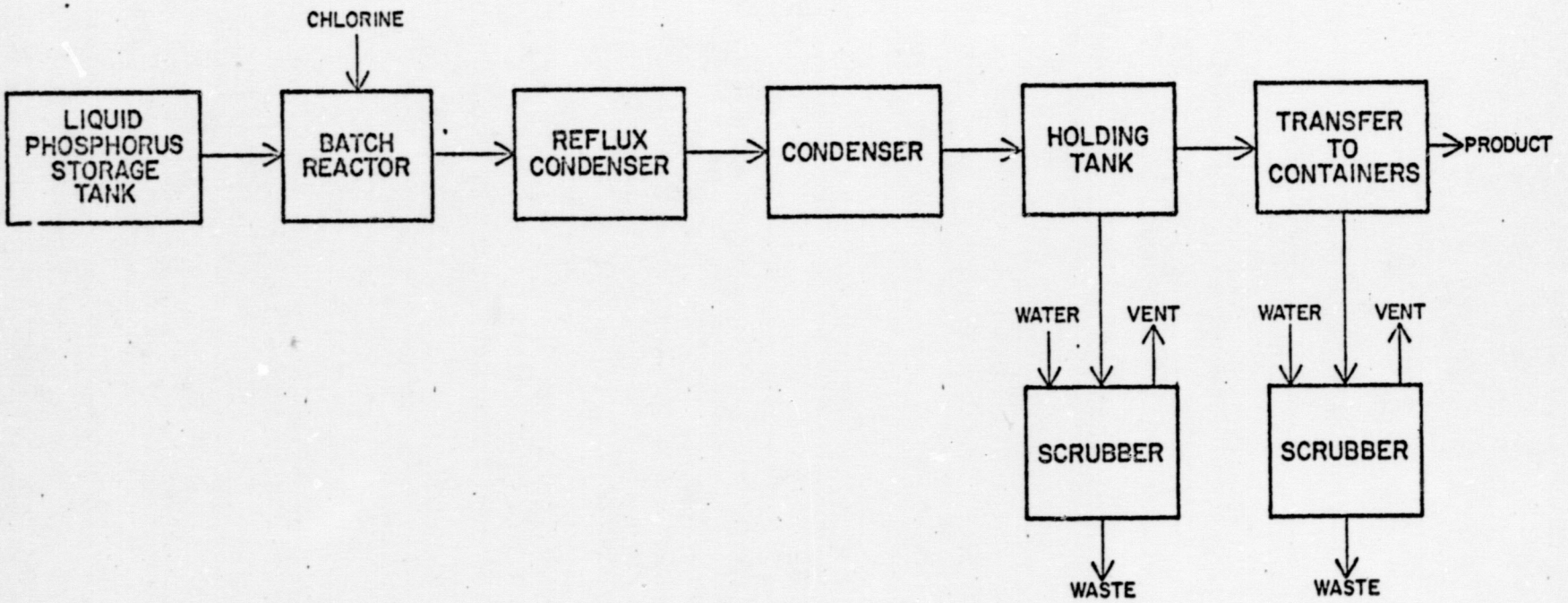

FIGURE 7
PHOSPHORUS TRICHLORIDE MANUFACTURE FLOW DIAGRAM

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When the reaction is complete, the cooling water to the reflux condenser is turned off, steam is supplied to the reactor jacket, and the product of the batch distillation is condensed and collected.

A water scrubber collects hydrochloric acid and phosphorous acid, the hydrolysis products of PCl_3 vapors:

$$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$$

The vapor pressure of the product is sufficiently high so that the fumes from transferring the product into shipping containers are also collected and scrubbed.

In a variation of the standard process, the reaction is conducted semi-continuously instead of batch-wise. The reflux condenser of Figure 7 is tailored so that only a small fraction of the PCl_3 is withdrawn as product; the larger fraction of condensed PCl_3 returns to the reactor and serves as the working fluid and heat sink for the reaction, since elemental phosphorus is somewhat soluble in PCl_3. Gaseous chlorine is added continuously, and liquid phosphorus is added incrementally.

No provision is generally made for continuous or frequent withdrawal of residue from the reactor either in the batch process or in the semi-continuous process. Instead, the residue is permitted to accumulate, and the reactor is shut down for cleanout at infrequent intervals.

Phosphorus trichloride is corrosive and is often shipped in returnable nickel drums. Prior to reuse, these drums are thoroughly washed with water and steam-cleaned. Some recent use has been made of non-returnable epoxy-lined steel drums.

~~2.2.5~~ Phosphorus Oxychloride

Phosphorus oxychloride, used in the preparation of organic phosphate esters and pharmaceuticals, is manufactured by the reaction of liquid phosphorus trichloride, chlorine, and solid phosphorus pentoxide:

$$3\ PCl_{3(\ell)} + 3\ Cl_{2(g)} + P_2O_{5(s)} \rightarrow 5\ POCl_{3(\ell)}$$

The standard process, illustrated in Figure 8, is carried out in a batch

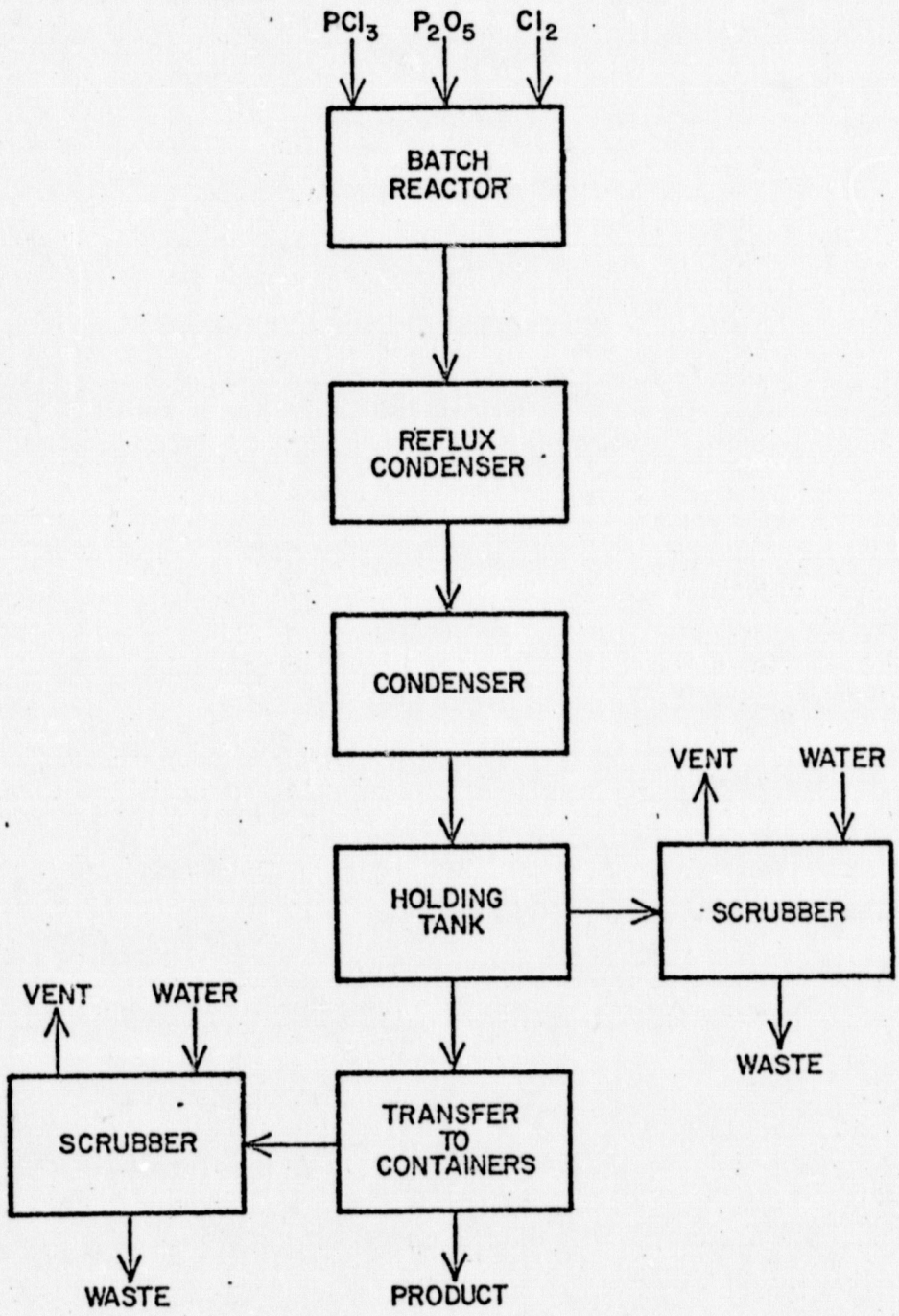

FIGURE 8
STANDARD PROCESS FOR
PHOSPHORUS OXYCHLORIDE MANUFACTURE

reactor and still very similar to the standard phosphorus trichloride equipment. Liquid phosphorus trichloride is charged to the reactor, solid phosphorus pentoxide is added, and chlorine is bubbled through the mixture while the PCl_3 (boiling point 74°C (165°F)) and later the $POCl_3$ (boiling point 105°C (221°F)) are refluxed. When the reaction is complete, steam is supplied to the reactor jacket, the water to the reflux condenser is shut off, and the product is distilled over and collected.

An alternate process for the manufacture of phosphorus oxychloride from phosphorus trichloride is also in commercial use. As is shown in Figure 9, dried air is used as the oxidant in a batch process. A water-cooled reflux condenser is used as in the standard process, except that a refrigerated condenser is added in series to ensure total reflux of the PCl_3 upstream of a water scrubber for the tail gas. The significant difference is that in the air-oxidation process, a large quantity of non-condensible gas (nitrogen and excess oxygen) is involved.

Instead of a final distillation step, the product $POCl_3$ is filtered, with periodic changing of the cartridge filter elements.

Water scrubbers collect hydrochloric acid and phosphoric acid, the hydrolysis products of $POCl_3$ vapors, from both the reaction/distillation equipment and from transferring operations (for either process):

$$POCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_4 \quad .$$

Like phosphorus trichloride, phosphorus oxychloride is extremely corrosive and is shipped in returnable nickel drums. Prior to reuse, these drums are thoroughly washed with water and steam-cleaned. Some recent use has been made of non-returnable epoxy-lined steel drums.

2.3 The Phosphate Segment

2.3.1 Sodium Tripolyphosphate

Sodium tripolyphosphate is manufactured by the neutralization in mix tanks of phosphoric acid by soda ash or by caustic soda and soda ash, with the subsequent calcining of the dried mono- and di-sodium phosphates crystals. Figure 10 is a flow diagram of the standard process. The sodium tripolyphosphate product is widely used in detergents and in water-softening applications.

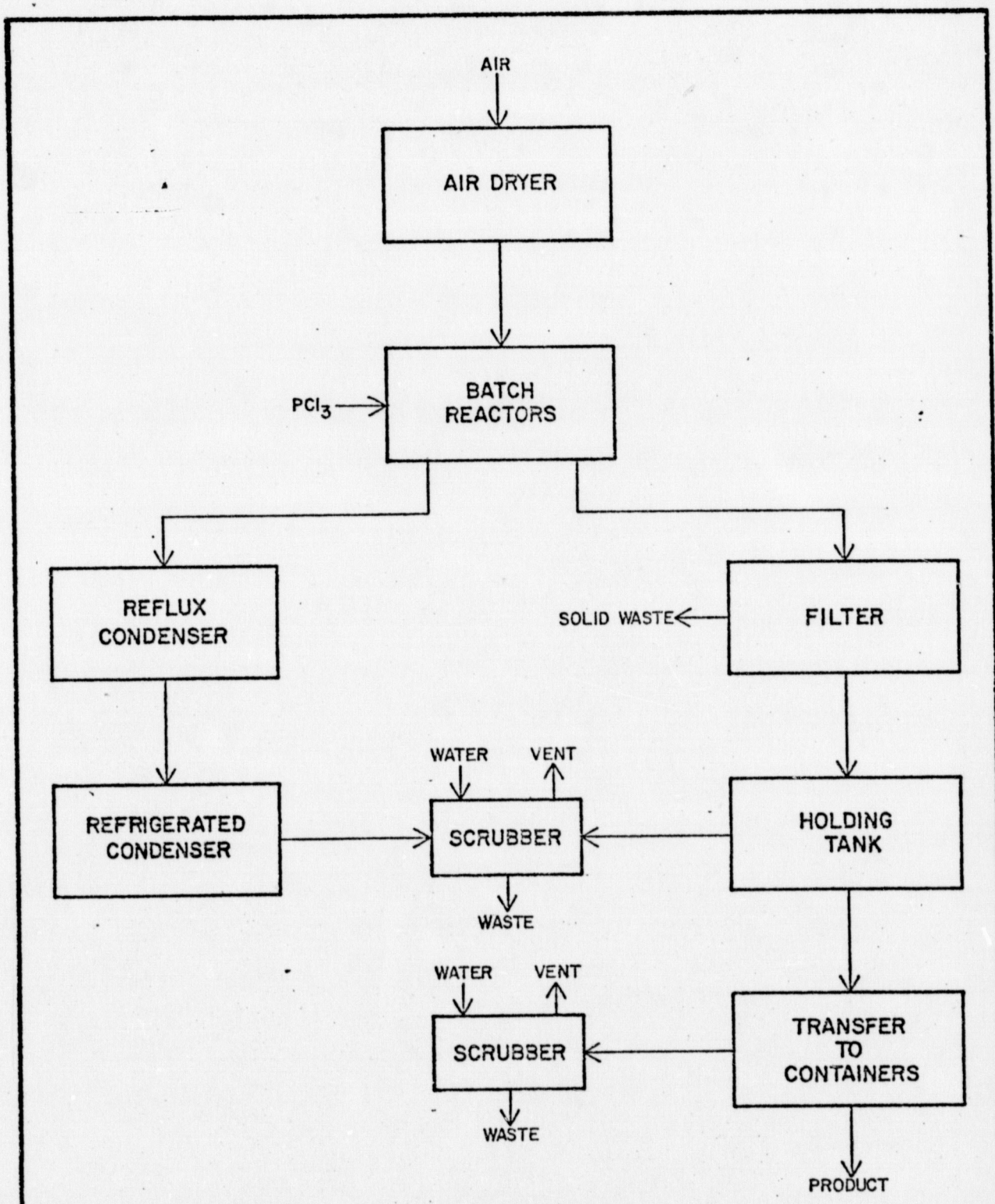

FIGURE 9
ALTERNATE PROCESS FOR
PHOSPHORUS OXYCHLORIDE MANUFACTURE

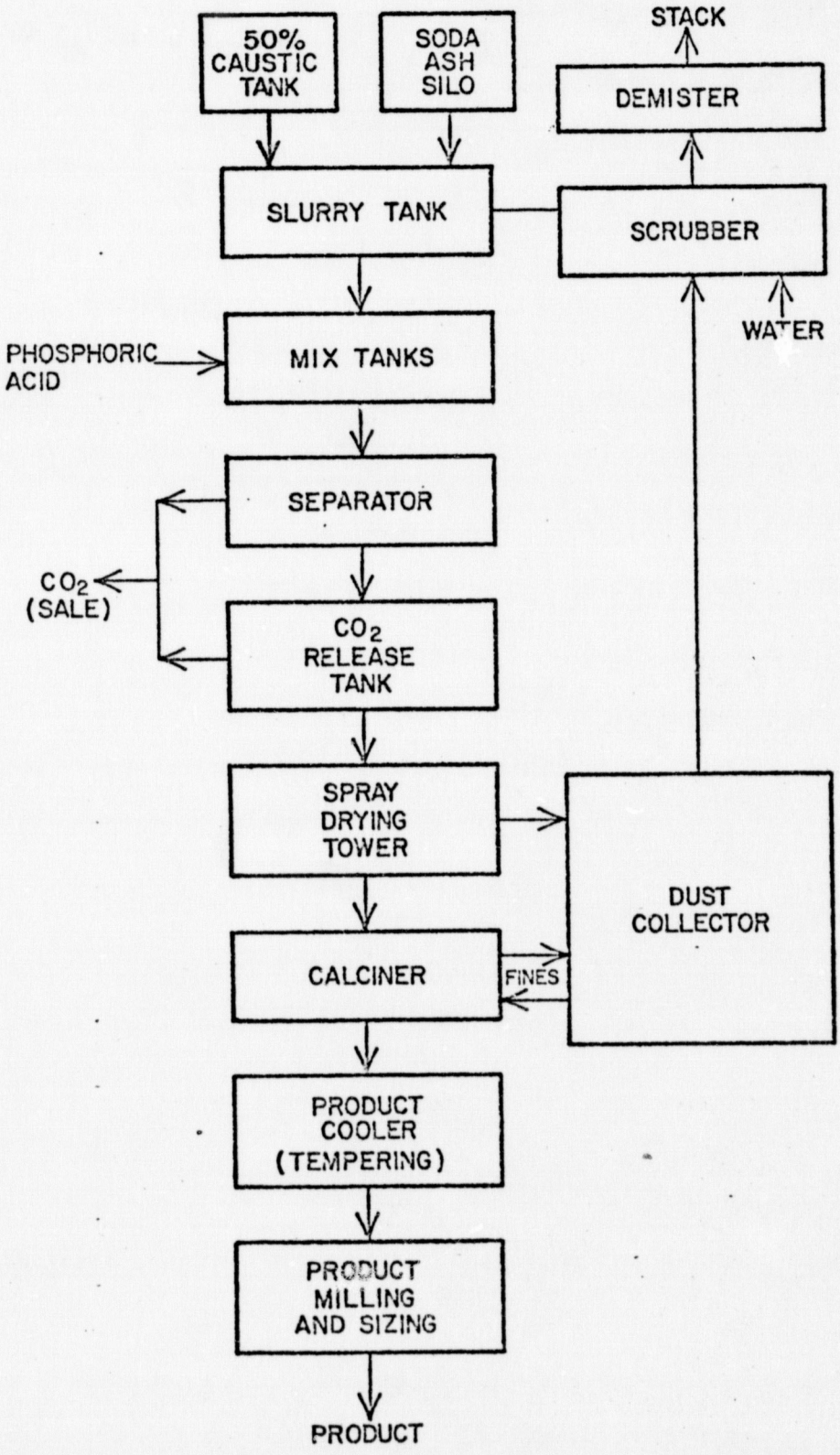

FIGURE 10
STANDARD PROCESS FOR
SODIUM TRIPOLYPHOSPHATE MANUFACTURE

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In the neutralization step, the amount of raw materials is measured and controlled to yield monosodium orthophosphate and disodium orthophosphate in a 1:2 mole ratio:

$$6H_3PO_4 + 5Na_2CO_3 \rightarrow 2NaH_2PO_4 + 4Na_2HPO_4 + 5H_2O + 5CO_2 ,$$

or

$$9H_3PO_4 + 5NaOH + 5Na_2CO_3 \rightarrow 3NaH_2PO_4 + 6Na_2HPO_4 + 10H_2O + 5CO_2$$

In either process variation, the final pH in the mix tank is very carefully adjusted by small additions of either phosphoric acid or caustic soda solution.

The mixture of sodium orthophosphates is spray-dried or drum-dried and the solids calcined to produce the sodium tripolyphosphate:

$$NaH_2PO_4 + 2\ Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2\ H_2O$$

The product is then slowly cooled or tempered to preserve the condensed form of the phosphates. If the product is chilled too rapidly, it will revert to a mixture of the meta- and pyrophosphates:

$$Na_5P_3O_{10} \rightarrow NaPO_3 + Na_2P_2O_7$$

~~2.3.2~~ Calcium Phosphates

The non-fertilizer calcium phosphates are made by the neutralization of phosphoric acid with lime. Although the reactions are chemically similar, the process for manufacturing the different calcium phosphates differ substantially from one another in the amount and type of lime used and the amount of process water used (See Figures 11 and 12).

a. Relatively pure, food-grade monocalcium phosphate (MCP) is made in a stirred batch reactor from furnace acid and lime slurry:

$$2H_3PO_4 + Ca(OH)_2 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + H_2O$$

An excess of phosphoric acid maintained during the batch addition cycle inhibits the formation of dicalcium phosphate. A minimum quantity of process water is used. The heat of reaction liberates some water as steam in the reactor, and the remaining water is evaporated in a vacuum dryer, a steam-heated drum dryer, or in a spray-dryer.

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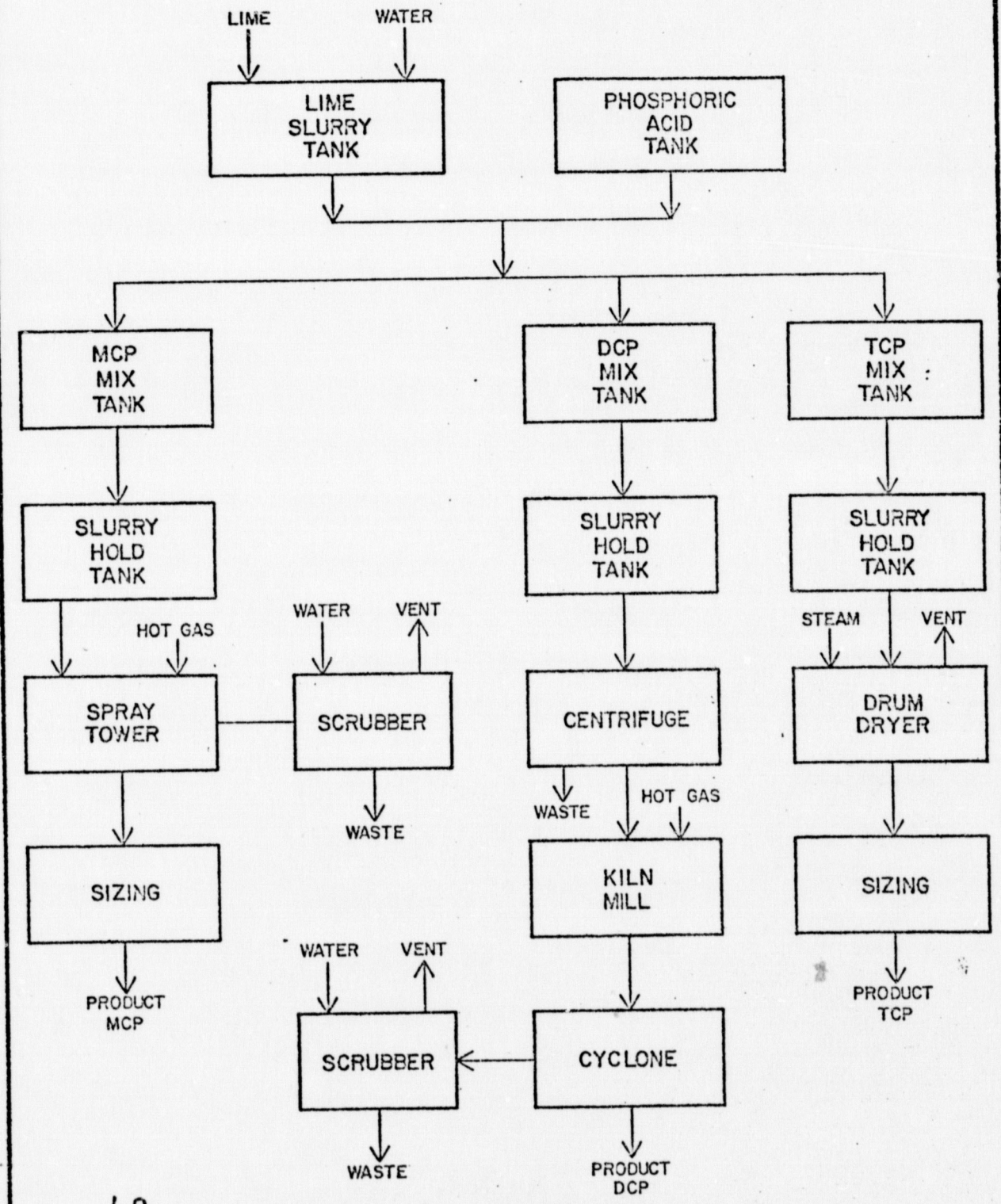

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FIGURE 11
STANDARD PROCESS FOR
FOOD-GRADE CALCIUM PHOSPHATES

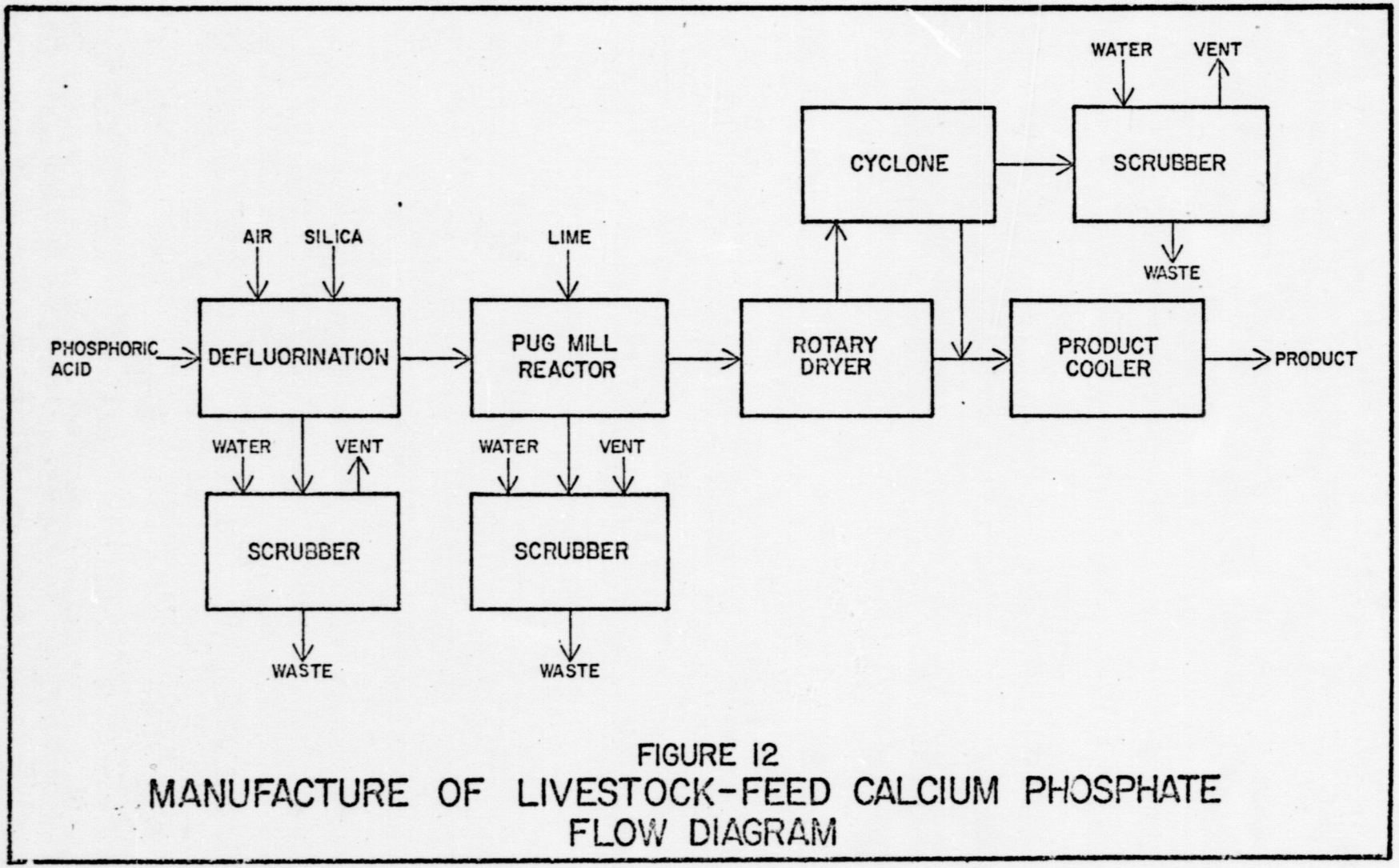

FIGURE 12
MANUFACTURE OF LIVESTOCK-FEED CALCIUM PHOSPHATE
FLOW DIAGRAM

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The anhydrous MCP is produced by using CaO (quicklime) and in carrying out the reaction at 140°C (310°F) so that water is driven off as it is produced.

b. Relatively pure, food-grade tricalcium phosphate (TCP) is made in a similar manner to MCP, except that an excess of lime slurry maintained during the batch addition cycle inhibits formation of dicalcium phosphate:

$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + 6H_2O$$

Like MCP, the TCP is dried so as to prevent excessive product temperatures.

c. Relatively pure, food-grade dicalcium phosphate (DCP) is made in batch stirred reactors, but with much more process water than for either MCP or TCP:

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 \cdot 2H_2O$$

The stoichiometry for DCP manufacture is critical; any excess H_3PO_4 during the batch addition cycle would result in some MCP and any excess $Ca(OH)_2$ would result in some TCP. The excess water in the DCP reactor is to ensure homogeneity so that the local stoichiometry is as balanced as the overall reactor stoichiometry.

As a result of the excess of water used, the reaction mixture is a pumpable slurry as opposed to the pasty consistency for MCP and TCP. This DCP is mechanically dewatered prior to drying.

d. Dicalcium phosphate (DCP) is also manufactured for livestock feed supplement use, with much lower specifications on product purity. Hence, the reaction can be conducted without excess water, since some MCP and/or TCP in the DCP product is perfectly tolerable. The pasty reaction product is normally dried in a rotary dryer. Powdered limestone, $CaCO_3$, may be used instead of lime. If quicklime is used, the drying step may be bypassed.

Another significant process difference is that non-food grade wet-process phosphoric acid is normally used for this product. The DCP plants defluorinate the acid unless this step was accomplished by the acid producer. Wet-process phosphoric acid contains approximately one percent fluoride in various forms. The defluorination consists of treating the heated acid with finely-divided silica and steaming or aerating, which liberates silicon tetrafluoride gas:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Wet scrubbers then hydrolyze and collect this gas as fluosilicic acid and silicic acid:

$$3\ SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3$$

The hot defluorinated phosphoric acid is then charged to the reactor to make dicalcium phosphate.

SECTION V

WATER USE AND WASTE CHARACTERIZATION

1.0 INTRODUCTION

With the background of manufacturing technology discussed in the previous Section, this Section discusses the specific water uses in the non-fertilizer phosphorus chemicals industry and the raw wastes from this industry prior to control and/or treatment of these wastes. Both Section IV and Section V are intended to be generally descriptive of the industry; i.e., they outline the standard manufacturing processes and the standard raw waste loads that are common to the great bulk of plants in the industry. It is not until Section VII, Control and Treatment Technology, and Section IX, Best Practicable Control Technology Currently Available, that distinctions are made (and quantitatively supported by independently-verified sampling data of plant effluents) within the industry, pointing out those exemplary plants which have already achieved significant reduction or total elimination of polluting discharges.

The discussion to follow in this Section, therefore, should not be taken as implying that the raw waste loads quoted are always actual plant discharges. Rather, they are intended to describe the total waste management problem originally faced by any plant in the industry. In actuality, significant abatement steps have been taken by some plants within the industry; by fully explaining the total waste management problem (in terms of raw waste loads), the control and treatment steps can be later explained and evaluated.

2.0 SPECIFIC WATER USES

Water is primarily used in the non-fertilizer phosphorus chemicals industry for eight principal purposes:

Non-contact cooling water
Process and Product Water
Transport Water
Contact Cooling or Heating Water
Atmospheric Seal Water
Scrubber Water
Auxiliary Process Water
Miscellaneous Uses

2.1 Non-Contact Cooling Water

Water used without contacting the reactants, such as in a tube-in-shell heat exchanger, is not contaminated with process effluent. If, however, the water contacts the reactants, then contamination of the water results and the waste load increases. Probably the single most important process waste control technique, particularly for subsequent treatment feasibility and economics, is segregation of non-contact cooling water from process water.

Non-contact cooling water is generally of two types in the industry. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is once-through cooling water whose source is generally a river, lake or tidal estuary, and the water is returned to the same source from which it was taken.

The only waste effluent from the recycled water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from the once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling tower blowdown may contain phosphates, nitrates, nitrites, sulfates and chromates. The water treatment chemicals may consist of alum, hydrated lime, and alkali metals such as sodium and potassium produced by ion exchange units. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid, depending upon the type of unit employed in the plant.

2.2 Process and Product Water

The process or product water generally is that which comes in contact with the product and stays with the product as an integral part, such as the quenching, hydrolysis and dilution water used in phosphoric acid manufacture, or the water used as a reaction medium in food-grade dicalcium phosphate manufacture.

2.3 Transport Water

Water may be used for transporting reactants or products between unit operations. A pure example is in the use of water for transferring (by displacement) liquid phosphorus. Another example is the transfer of electrostatic precipitator dust in phosphorus manufacture as a slurry in water.

Since intimate contact between the process materials and transport water occurs, this water may generally contain dissolved or suspended materials and so is classified as process water.

2.4 Contact Cooling or Heating Water

This water comes under the general heading of process water because it comes in direct contact with process waters. A prime example is the large quantity of water used to quench the slag from phosphorus furnaces; another is the water used to condense the gaseous phosphorus after it is produced in the furnaces.

Other direct contact cooling or heating water usage such as that for contact steam heating and/or drying, steam distillation, pump and furnace seals, etc., is generally of much lower volume than the barometric condenser water and is easier to treat for waste effluents.

2.5 Atmospheric Seal Water

Because some of the materials in this industry spontaneously ignite upon contact with air, the air is kept out of reaction vessels using a water seal. Liquid phosphorus is universally protected by storing under a water blanket. These seal waters are considered as process waters.

2.6 Scrubber Water

Throughout this industry, water scrubbers are used to remove process vapors and/or dusts from tail gases or from gaseous process streams. The used scrubber water is regarded as process water since direct and intimate contact has occurred; the resultant solution or suspension may contain impurities or may be too dilute a solution to reuse or recover and thus is discharged.

2.7 Auxiliary Process Water

This water is used in medium quantities by the typical plant for auxiliary operations such as ion exchange regenerants, make-up water to cooling towers with a resultant cooling tower blowdown, make-up water to boilers with a resultant boiler blowdown, equipment washing, storage and shipping tank washing, and spill and leak washdown. The volume of waste water from these operations is generally low in quantity but highly concentrated in effluents.

2.8 Miscellaneous Water Uses

These water uses vary widely among the plants with general usage for floor washing and cleanup, safety showers and eye wash stations, sanitary uses, and storm run-off. The resultant streams are either non-contaminated or slightly contaminated with wastes. The general practice is to discharge such streams without treatment except for sanitary waste.

3.0 PROCESS WASTE CHARACTERIZATION

The descriptions of the manufacturing processes in Section IV, and the flow diagrams included in that Section, qualitatively discussed the sources of wastes. The following discussion is intended to quantify these waste streams both in quantity and in composition. These waste streams are the "raw" wastes prior to control or treatment (which is separately discussed in Section VII).

Aqueous wastes emanating from air pollution abatement equipment are considered as process wastes in this study.

The following sections quantify the raw process wastes in each segment of the industry. A discussion of the source, nature, and amount of these wastes for each segment is followed by a table summarizing the standard raw waste load.

Various plants in the industry differ significantly in the degree of process and cooling water recirculation. Hence, the wastewater quantities and constituent concentrations quoted may be grossly different from plant-to-plant. However, the raw waste loads in kg per kkg of product (lbs/ton) are dependent primarily upon the manufacturing processes and are therefore much more representative of the entire industry.

3.1 The Phosphorus Production Segment

The discussion of phosphorus manufacturing technology in Section IV and the flow diagram of Figure 2, qualitatively pointed out the following streams emanating from the process (in addition, of course, to the phosphorus product stream):

By-products: Slag, Ferrophosphorus, and Carbon Monoxide
Non-contact Cooling Water

Electrostatic Precipitator Dust
Calciner Precipitator Dust
Calciner and Furnace Fume Scrubber Liquor
Phosphorus Condenser Liquor (Aqueous phase)
Phosphorus Sludge (or mud)
Slag Quench Liquor

The following sections discuss each of the above in quantitative detail, and identify which are typically returned to the process and which are classified as raw waste streams from the manufacturing operation.

3.1.1 By-product Streams

The by-products of the phosphorus manufacturing operation are:[4,9,10]

	kg/kkg	lb/ton
Ferrophosphorus	300	600
Slag ($CaSiO_3$)	8,900	17,800
CO gas	2,800	5,600

Both ferrophosphorus and slag are sold, and the carbon monoxide is either used to generate heat in the process or is otherwise burned on site. Hence, none of the above three materials is considered a waste.

The quench water used for the by-product slag is separately discussed as a waste stream.

The by-product ferrophosphorus is cast as it is tapped from the furnace and air-cooled. The solids are then broken up and shipped. No water is used specifically for ferrophosphorus, and there are no wastes accountable for ferrophosphorus manufacture.

3.1.2 Non-Contact Cooling Water

Phosphorus production facilities generate huge quantities of heat. The electrical power consumption is approximately 15,500 kwh/kkg (48 million Btu/ton).[6,9,10] An additional 8,100 kwh/kkg (25 million Btu/ton) are generated by combustion of the by-product carbon

monoxide. Some of this energy, 6,100 kwh/kkg (19 million Btu/ton), is absorbed in the endothermic furnace reaction, and some is absorbed by the endothermic calcining operation. Other portions of this energy are released to the atmosphere by burning of waste carbon monoxide (that not used for calcining) and by convection, radiation and evaporative losses from the equipment and process materials. Still other portions are absorbed by contact waters in the calcining and furnace from scrubbers, in the phosphorus condenser, and in the slag quenching operation.

After accounting for the above energy demands, a significant quantity of heat is absorbed by non-contact cooling water for the furnace shell, the crucible bottom, the fume hood, the tap holes, the electrode fixtures, the electrical transformer, and for any indirect phosphorus condensation. The quantity of this water is highly variable from plant-to-plant, and depends upon the furnace design, the furnace size, the degree of recirculation (through heat exchangers with other water streams or through cooling towers), whether or not cooling water is used in series for different requirements, the inlet temperature of the available cooling water, and the ambient air temperature. Plant 181 uses 325,000 l/kkg of product (78,000 gal/ton); Plant 159 uses 38,000 l/kkg (9,000 gal/ton); and TVA at Muscle Shoals, Alabama,(5) uses 130,000 l/kkg (31,000 gal/ton).

3.1.3 Electrostatic Precipitator Dust

The high-temperature electrostatic precipitator removes dusts from the furnace gases before these gases are condensed for recovery of phosphorus. These dusts may contain up to 50 percent P_2O_5,(4) and therefore finds value either as a fertilizer for sale or for return to the process. In the latter case, it is transported to the ore-blending head end of the plant. One TVA scheme slurries the dust for transport; the slurry is pumped to a settling pond, the settled solids are fed to the ore-blending unit, and the pond overflow is reused in the slurrying operation.(7,9)

The quantity of precipitator dust is approximately 125 kg/kkg of product (250 lb/ton).(9) Regardless of the method of sale or reuse, the precipitator dust is not a waste material to be disposed of from the plant.

3.1.4 Calciner Precipitator Dust

Dry dust collectors are used in the calcining operation, upstream

of wet scrubbing systems. The dry fine dusts collected are recycled directly to the sizing and calcining operations. The collected and recycled fines may amount to as much as 30 per cent of the net production from the nodulizing process.(10)

There is no plant discharge of dry calciner precipitator dusts; therefore this is not a component of the plant's raw waste load.

3.1.5 Calciner and Furnace Fume Scrubber Liquor

Water scrubbers are used for air-pollution abatement for the calciner exhaust stream (downstream of dry dust collection), for furnace fumes, for ore sizing dusts, for coke handling dusts, for raw material feeding operation dusts, and for furnace taphole (slag and ferrophosphorus) fumes. The scrubber liquor contains suspended solids (which are mainly SiO_2 and Fe_2O_3), some phosphates and sulfates as dissolved solids, and a large quantity of fluorides. To explain the presence of these fluorides in the scrubber liquor, Table 4 lists the quantities of materials in commercial phosphate rock, derived from analyses published by Kirk and Othmer,(12) and presented as pounds per ton of phosphorus ultimately produced after normalizing to 26 percent P_2O_5 content. From Table 4, the average quantity of F in ore is 275 kg/kkg of P_4 (550 lbs/ton). Approximately 8 percent of this quantity of F, or 22 kg (44 lbs), is volatilized in the ore calcining operation,(7) and is subsequently a constituent of the scrubber liquor.

This scrubber liquor is highly acidic for three reasons: the sulfur (as SO_3) forms sulfuric acid: the P_2O_5 forms phosphoric acid; and the fluorine, which is released in the form of silicon tetrafluoride, forms fluosilicic acid and silicic acid upon hydrolysis.

The quantity of scrubber liquor wasted depends upon the degree of recirculation of this liquor from a sump back to the scrubbers. TVA at Muscle Shoals(5) circulates approximately 21,000 l/kkg of product (5,000 gal/ton) with a portion bled off to control the composition. This scrubber liquor is of the following composition:(7)

Constituent	Concentration, %
F	3.1
SiO_2	1.1
P_2O_5	0.2
Fe_2O_3	0.1
S	1.7

TABLE 4

Composition of Commercial Phosphate Rocks

Expressed as kg per kkg (lbs/ton) of Phosphorus Produced

Constituent	Florida Land Pebble Furnace Grade		Tennessee Brown Rock Furnace Grade		Western Phosphoric Rock Low Grade	
	kg/kkg	lbs/ton	kg/kkg	lbs/ton	kg/kkg	lbs/ton
P_2O_5	2,600	5,200	2,600	5,200	2,600	5,200
CaO	3,800	7,600	3,550	7,100	3,150	6,300
MgO	35	70	75	150	190	380
Al_2O_3	125	250	1,230	2,460	810	1,620
Fe_2O_3	155	310	760	1,520	550	1,100
SiO_2	725	1,450	3,150	6,300	3,750	7,500
SO_3	215	430	50	100	260	520
F	305	610	270	540	245	490
CO_2	330	660	150	300	550	1,100
Organic Carbon	40	80	35	70	685	1,370
Na_2O	10	20	35	70	205	410
K_2O	10	20	50	100	135	270

If the fluoride concentration of 3.1 percent is equated to a standard raw waste load (as previously discussed) of 22 kg/kkg (44 lbs/ton), the quantities of other scrubber liquor components may be calculated:

Constituent	Raw Waste Load	
	kg/kkg	lbs/ton
F	22	44
SiO_2	8	16
P_2O_5	1.5	3
Fe_2O_3	0.5	1
S	12	24

The total $CaCO_3$ acidity of the scrubber liquor, calculated from the above constituent quantities, is 60 kg/kkg (120 lbs/ton).

Other plants do not recirculate scrubber liquor; the volume wasted is much greater and the constituent concentrations are much smaller, but the raw waste loads (in kg/kkg of product) should be comparable. Plant 181 does not directly recirculate the liquor, and uses 300,000 l/kkg (71,000 gal/ton) for scrubbing.

3.1.6 Phosphorus Condenser Liquor

The furnace gases pass from the electrostatic dust precipitator to the phosphorus condenser, where a recirculating water spray condenses the product. This condenser liquor is maintained at approximately 60°C (140°F), high enough to prevent solidification of the phosphorus (freezing point 44°C (112°F)). This condenser liquor is "phossy water" essentially a colloidal dispersion of phosphorus in water, since the solubility at 20°C (68°F) is only 3.0 ppm. Depending upon how intimate the water-phosphorus contact was, the phosphorus content of phossy water may be as high as several weight per cent.(5)

The condenser liquor also contains constituents other than elemental phosphorus: fluoride, phosphate, and silica. Using the average F content of ore (from Table 4) of 275 kg/kkg, plus the estimate that 12 per cent of the F in the ore volatilizes in the furnace(4,7) and is there-

fore equivalent to 33 kg/kkg (66 lbs/ton), and by accounting for 6 kg of F per kkg (12 lbs/ton) which is collected in the precipitator dust and in the phosphorus sludge ash;(7) a raw waste load of F is derived of 27 kg/kkg (54 lbs/ton) in the condenser liquor. This condenser liquor is not acidic despite the hydrolysis of P_2O_5 and SiF_4 to H_3PO_4, H_2SiF_6, and H_2SiO_3 because aqueous ammonia or caustic is added to prevent undue corrosion in the condenser.

There are other sources of phossy water within the plant. Storage tanks for phosphorus have a water blanket, which is discharged upon phosphorus transfer. Railroad cars are cleaned by washing with water. Phosphorus may be purified by washing with water. Together, all sources of phossy water wastes amount to about 5,400 l/kkg (1,300 gal/ton), and at a concentration of 1,700 ppm, the quantity of phosphorus wastes amount to about 9 kg/kkg produced (18 lbs/ton), as reported by TVA.(5)

At TVA, the condenser liquor is recirculated at the rate of 33,000 l/kkg (8,000 gal/ton).(8,9) Other plants may differ significantly in the quantity of phossy water circulated, but the raw wastes (in kg/kkg of product) should be fairly uniform. For example, Plant 181, which does not directly recirculate its condenser water, uses 84,000 l/kkg (20,000 gal/ton), with an additional 17,000 l/kkg (4,000 gal/ton) for phosphorus handling and storage.

To calculate the raw waste loads of phosphate and silica in the condenser liquor, the following TVA recirculated-liquor composition was used:(7)

Constituent	Concentration, %
F	8.3
P_2O_5	5.0
SiO_2	4.2

Equating 8.3 per cent F with the previously-derived 27 kg/kkg of F, the raw waste loads of P_2O_5 and SiO_2 become (respectively) 16.5 kg/kkg (33 lbs/ton) and 13.5 kg/kkg (27 lbs/ton).

3.1.7 Phosphorus Sludge

In addition to phossy water, the phosphorus condenser sump also collects

phosphorus sludge, which is a colloidal suspension typically 10 per cent dust, 30 per cent water and 60 per cent phosphorus.(8) The quantity of sludge formed is directly dependent upon the quantity of dust that escapes electrostatic precipitation; hence the very large investment made for highly-efficient precipitators.

Using 125 kg of dust (per kkg of product) collected by the electrostatic precipitator,(9) and assuming a 98 per cent collection efficiency,(10) the dust reaching the condenser amounts to 2.5 kg/kkg. If all of this dust became part of the sludge, the sludge quantity would be 25 kg/kkg (50 lbs/ton) of product, and it would contain 15 kg/kkg (30 lbs/ton) of elemental phosphorus.

This sludge is then universally processed for recovery of phosphorus, typically by centrifugation. A 96 percent recovery has been reported, with the product (subsequently returned to the process) averaging 92 to 96 per cent phosphorus.(8) The remaining 4 per cent of the phosphorus in the sludge is burned in a phosphoric acid unit, so that no wastes emanate from the plant.

Other methods for processing the sludge which also result in no plant effluent include heating in a slowly rotating drum in an inert atmosphere to drive off phosphorus vapor, which is then condensed with a water spray into a sump. The solid residue obtained is completely free of elemental phosphorus and can be safely landfilled or recycled to the feed preparation section of the plant.(10)

3.1.8 Slag Quenching Liquor

Slags from phosphorus furnaces are mainly SiO_2 and CaO, and would also contain Al_2O_3, K_2O, Na_2O, and MgO in amounts consistent with the initial ore composition. In addition to these oxides, phosphate rock may contain 0.2 to 0.4 pound of uranium per ton of ore,(4) and the radiation levels of both the slag and the quench waters must be appropriately noted. Other constituents of the slag presenting problems for quench water pollution control are fluoride and phosphate. Approximately 80 per cent of the original F in the phosphate rock, 220 kg/kkg of P_4 (440 lbs/ton), referring to Table 4, winds up in the slag.(4) About 2.7 per cent of the original P_2O_5 in the phosphate rock, 70 kg/kkg (140 lbs/ton), winds up in the slag.(4)

At Plant 181, approximately 24,600 l/kkg (5,900 gal/ton) may be used for quenching the slag, with the slag quench liquor having the following composition(24) and raw waste loads:

Constituent	Concentration, ppm	Raw Waste Load kg/kkg P_4	Raw Waste Load lbs/ton P_4
Total Suspended Solids	800	20	40
Total Dissolved Solids	1,700	42	85
Phosphates (as P)	12	0.3	0.6
Sulfate (as S)	1,000	25	50
Fe	14	0.35	0.7
F	170	4.5	9
Total Alkalinity	230	5.5	11

TABLE 5

Summary of Raw Wastes from Phosphorus Manufacture

Note: Wastewater Quantities and Constituent Concentrations are highly variable, depending upon degree of recirculation, but the raw waste loads should be representative.

	Calciner Scrubber Liquor	Phosphorus Condenser Plus Other Phossy Water	Slag Quenching Water	Composite Waste
Wastewater Quantity, l/kkg	300,000	100,000	25,000	425,000
gal/ton	72,000	24,000	6,000	102,000
Raw Waste Load, kg/kkg				
TSS	8.5	13.5	20.5	42.5
P_4	-	9	-	9
PO_4	2	22	1	25
SO_4	36	-	75	111
F	22	27	4.5	53.5
Total Acidity	60	-	-	54.5
Total Alkalinity	-	-	5.5	-
Raw Waste Load, lbs/ton				
TSS	17	27	41	85
P_4	-	18	-	18
PO_4	4	44	2	50
SO_4	72	-	150	222
F	44	54	9	107
Total Acidity	120	-	-	109
Total Alkalinity	-	-	11	-
Concentrations, ppm				
TSS	28	135	820	100
P_4	-	90	-	21
PO_4	7	220	40	59
SO_4	120	-	3,000	260
F	73	270	180	126
Total Acidity	200	-	-	128
Total Alkalinity	-	-	220	-

3.2 The Phosphorus-Consuming Segment

No direct process aqueous wastes are generated in this segment of the industry. The raw wastes arise from phosphorus storage and transfer, from wet scrubbing of tail gases, from vessel cleaning, and from leaks and spills.

3.2.1 Phossy Water Wastes

Because phosphorus is transported and stored under a water blanket, phossy water is a raw waste material at phosphorus-using plants as well as at phosphorus-producing plants. The standard procedure when liquid phosphorus is transferred from a rail car to the using plant's storage tank is to pump the displaced phossy water from the storage tank back into the emptying rail car.(8,18,26) Instead of being wasted at the phosphorus-using plant, the phossy water is shipped back to the phosphorus-producing facility for treatment and/or reuse. Therefore, standard raw phossy water wastes at the phosphorus-using plants are due to surges or to anomalies in the storage tank water level control system rather than to the direct wasting of all displaced water.

A more insidious source of phossy water may arise at phosphorus-consuming plants. Should reactor contents containing phosphorus ever be dumped into a sewer as a result of operator error, emergency conditions or inadvertent leaks or spills, the phosphorus would remain at the low points in the sewer line generally as a solid (melting point 44°C (111°F)) and would contact all water flowing in that sewer from that time on. Since phosphorus burns when exposed to air (autoignition temperature 93°F), there is general reluctance to clean it out; the common practice is to ensure a continuous water flow to prevent fire.

The typical phosphorus loss for phosphorus-consuming plants is 1 kg lost to phossy water per kkg consumed (2 lbs/ton).(22) Whenever phosphorus is transferred by displacement, 580 liters of water are displaced per kkg of phosphorus (140 gal/ton). These values are equivalent to a phosphorus concentration of 1700 ppm. For comparison, a typical phosphorus content in phossy water at a phosphorus-producing plant has also been reported at 1700 ppm.(5)

3.2.2 Phosphoric Acid Manufacture

The production of phosphoric acid by the "dry" process from elemental

phosphorus consumes a total of about 380 liters of water per kkg of product (92 gal/ton) for both the hydration and the acid dilution steps. The cooling water requirements are typically 92,000 liters per kkg of product (22,000 gal/ton); but with recycle of cooling water, the makeup cooling water requirement is approximately 4,600 liters per kkg of product (1,100 gal/ton).(20)

There is no aqueous process waste from exemplary phosphoric acid plants.(4,15,16,19,20) However, despite good housekeeping at an exemplary plant, leaks or spills of phosphoric acid may amount to an average of 1 kg/kkg (2 lbs/ton), with a range of 0 to 2.5 kg/kkg (0 to 5 lbs/ton). (16,19,20)

Where food-grade phosphoric acid is produced, a standard raw waste of 0.1 kg/kkg (0.2 lb/ton) of arsenic sulfide is precipitated by addition of a soluble sulfide (H_2S, Na_2S, NaHS), and filtered out of the acid. (19,20,21) An additional 0.75 kg/kkg (1.5 lbs/ton) of filter-aid material may accompany the sulfide as a solid waste.

3.2.3 Phosphorus Pentoxide Manufacture

The waste water from the tail seals on the condensing towers typically contain 0.25 kg/kkg (0.5 lb/ton) of H_3PO_4 (100 per cent basis).(22) Approximately 500 liters/kkg (120 gal/ton) of water may be used, resulting in a concentration of 470 ppm for the effluent bleed.

The inlet air dryer silica gel is regenerated often, but is renewed very infrequently (perhaps every ten years). The wasted material is typically landfilled.

Approximately 29,000 l/kkg (7,000 gal/ton) of non-contact cooling water is used.(22)

3.2.4 Phosphorus Pentasulfide Manufacture

The water seals on the batch reactor vent lines accumulate a mixture of phosphorus mud and lower phosphorus sulfides. These seals are cleaned once a week, and the residue amounts to 0.15 kg/kkg (0.3 lbs/ton). This residue is hazardous and flammable, and is typically buried.(22,26)

Should any batch be aborted (a rare occurrence) because of agitator failure, cast-iron pot failure or other reason, the material is disposed of by incineration.(22,26)

The dust collected by a cyclone from the P_2S_5 crushing operation amounts to 1 kg/kkg (2 lbs/ton).(22,26)

The still pot for the vacuum distillation step accumulates impurities, which include carbon and iron sulfur compounds and glassy phosphates. Most important, the residues contain arsenic pentasulfide, which is higher-boiling than the corresponding phosphorus pentasulfide. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton), of arsenic which is equivalent to 0.05 kg of As_2S_5 per kkg of product P_2S_5 (0.1 lb/ton). The entire still pot residue is about 0.5 kg/kkg (1 lb/ton). Periodically, these residues are removed and the solids are broken up and buried.(22,26) Approximately 17,000 l/kkg (4,000 gal/ton) of non-contact cooling water is used.(22)

In the casting of liquid P_2S_5, the fumes from burning liquid (molten P_2S_5 auto-ignited) are scrubbed. Typically, the scrubber water contains 1.25 kg of combined P_2O_5 amd SO_2 per kkg of product P_2S_5 (2.5 lbs/ton).(22) Because both P_2O_5 and SO_2 are absorbed by a water scrubber only with difficulty, the water flow rate is high, 30,000 l/kkg (7,200 gal/ton).(22) These values reduce to concentrations of PO_2^{3-} and SO_3^{2-} in the scrubber effluent of 17 and 34 ppm (respectively). Much lower scrubber flow rates could be used should weak caustic or lime be used instead of water.

3.2.5 Phosphorus Trichloride Manufacture

The batch or semicontinuous reactor/stills accumulate residues which are periodically but infrequently removed. These residues contain arsenic trichloride, which is higher-boiling than the corresponding phosphorus trichloride. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lbs/ton) of arsenic, which is equivalent to 0.05 kg of $AsCl_3$ per kkg of product PCl_3 (0.1 lb/ton). This is about half the quantity of total residue in the stills. (exclusive of residual PCl_3 from the last batch or run before shutdown).

The average non-contact cooling water requirement is 54,000 l/kkg (13,000 gal/ton).(18,22)

Water scrubbers collect PCl_3 vapors from the reaction, the product distillation, the product storage, and the product transfer operations, and hydrolyze these vapors to HCl and to H_3PO_3 (which may subsequently be oxidized to H_3PO_4). The quantity of PCl_3 collected is highly dependent upon the efficiency of the upstream condensers, since PCl_3 is highly volatile:

Temp, °C	Temp, °F	Vapor Pressure, mm Hg[27]
20	68	99
40	104	235
60	140	690
76	169	760

At Plant 037, sufficient heat transfer area was provided in the condensers to limit the raw waste load to 3 kg of HCl plus 2.5 kg of H_3PO_3 per kkg of product PCl_3 (6 lbs and 5 lbs/ton). Approximately 5,000 l/kkg (1,200 gal/ton) of scrubber water were used to collect these wastes. Other smaller waste quantities of HCl and H_3PO_3 generated from tank car and returnable container cleaning operations have been included in these quantities.

These quantities are based upon the most reliable data available at Plant 037; overall material balances of product PCl_3 shipped vs. elemental phosphorus received. These data, validated over long periods of time for profitability purposes, show a total loss of phosphorus trichloride of 5 kg/kkg (10 lbs/ton).(18) An estimated breakdown of this loss is:

Transfer and Storage of Phosphorus,	1.0 kg/kkg (2 lbs/ton)
Reactor/Still Residues,	0.1 kg/kkg (0.2 lb/ton)
Scrubber for Distillation Tail Gases,	2.5 kg/kkg (5 lbs/ton)
Transfer of PCl_3,	1.0 kg/kkg (2 lbs/ton)

Other than the estimated loss of elemental phosphorus and the reactor/still residues, the losses which become water-borne raw wastes amount to 3.5 kg/kkg (7 lbs/ton). Upon hydrolysis, this stoichiometrically becomes 3 kg/kkg (6 lbs/ton) of HCl plus 2.5 kg/kkg (5 lbs/ton) of H_3PO_3. These material-balance data have been used because of their long-term confirmation. Direct measurements of wastewater flowrates and of wastewater constituent analysis were not relied upon in this case since accurate flowrate measurements were not possible in the existing plant configuration and since no statistically-meaningful analytical data had been collected.

3.2.6 Phosphorus Oxychloride Manufacture

The water scrubber for the distillation operation in the standard process (using P_2O_5 and Cl_2) typically collects 1.5 kg of HCl (anhydrous

basis) and 0.25 kg of H_3PO_4 (100 per cent basis) per kkg of product $POCl_3$ (3 lbs and 0.5 lb/ton), and the scrubber for $POCl_3$ transferring collects about 0.2 kg of HCl and 0.15 kg of H_3PO_4 per kkg of product (0.4 lb and 0.3 lb/ton).(22) Allowing for small wastes from returnable container cleaning operations, the standard raw waste load is 2 kg of HCl and 0.5 kg of H_3PO_4 per kkg of product (4 lbs and 1 lb/ton).(22) Approximately 2,500 l/kkg (600 gal/ton) of water are used, so that the raw waste concentrations are 800 ppm HCl and 200 ppm H_3PO_4.

The source of the above data on raw waste loads was Plant 147 records and plant personnel analysis of these records. An independent verification of these results was not judged valid since at this plant neither an accurate determination of wastewater flowrate nor the collection of a distinct wastewater sample from each unit operation contributing to the waste load was practical; and since statistically-valid background data was not at hand.

These waste quantities for $POCl_3$ manufacture are somewhat smaller than for PCl_3 manufacture since $POCl_3$ is less volatile (boiling point 107°C). In the batch process, the refluxing liquid is all PCl_3 at the start, but becomes increasingly richer in $POCl_3$.

The air-oxidation process presents a much more difficult task for the reflux condenser, since the vapors are highly diluted with non-condensibles. However, with the use of refrigerated condensers, the measured raw waste load is no different for this process.(18) At Plant 037, data collected over three months from the reactor/still scrubber for $POCl_3$ manufacture, which had an estimated flowrate of 1,800 l/kkg (430 gal/ton), had average net values of:

Chloride	669 ppm
$CaCO_3$ acidity	1,213 ppm

These data reduce to a raw waste of 1.2 kg/kkg (2.4 lbs/ton) of HCl plus 0.35 kg/kkg (0.7 lbs/ton) of H_3PO_4; which are extremely close to the corresponding values for Plant 147.

Where product $POCl_3$ is filtered, the used filter elements are first washed to hydrolyze the residual $POCl_3$. Disposable elements are then landfilled. The quantity of filtered solids retained on the elements is only a very small fraction of the weight of the used element.(18) The elements are washed in a 55-gallon drum, so that a very small quantity of wastewater (and of acid wastes) is involved compared to the

scrubber waste load. Although there is no continuous withdrawal of residues from $POCl_3$ distillations, very little residue accumulates. Twice a year, this residue (mostly glassy phosphates) is washed out with hot water.(18,22)

The non-contact cooling water requirement for $POCl_3$ manufacture by either the standard or the alternate method is approximately 50,000 l/kkg (12,000 gal/ton).(18,22)

TABLE 6

Summary of Raw Wastes from Phosphorus-Consuming Plants

	H_3PO_4 (75%)	P_2O_5	P_2S_5	PCl_3	$POCl_3$
Phossy Water: P_4 conc, ppm	1,700	1,700	1,700	1,700	--
l/kkg P_4 consumed	580	580	580	580	--
kgP_4/kkg P_4 consumed	1	1	1	1	--
gal/ton P_4 consumed	140	140	140	140	--
lbs/ton P_4 consumed	2	2	2	2	--
Process Water Wasted: l/kkg Pdt	--	500	30,000	5,000	2,500
gal/ton Pdt	--	120	7,200	1,200	600
Raw Waste Load, kg/kkg Pdt:					
HCl	--	--	--	3	2
H_2SO_3	--	--	1	--	--
H_3PO_3 + H_3PO_4	1	0.25	0.5	2.5	0.5
Raw Waste Load, lbs/ton Pdt:					
HCl	--	--	--	6	4
H_2SO_3	--	--	2	--	--
H_3PO_3 + H_3PO_4	2	0.5	1	5	1
Concentrations, ppm: HCl	--	--	--	600	800
H_2SO_3	--	--	34	--	--
H_3PO_3 + H_3PO_4	High	470	17	500	200
Process Water Consumed: l/kkg Pdt.	380	--	--	--	--
gal/ton Pdt	92	--	--	--	--
Cooling Water Used: l/kkg Pdt	91,000	29,000	16,600	54,000	50,000
gal/ton Pdt	22,000	7,000	4,000	13,000	12,000
Solid Wastes, kg/kkg Pdt:					
As Compounds	0.1	--	0.05	0.05	--
Total Residues	--	--	0.7	0.05	<0.05
Solid Wastes, lbs/ton Pdt:					
As Compounds	0.2	--	0.1	0.1	--
Total Residues	--	--	1.4	0.1	<0.1

3.3 The Phosphate Segment

The aqueous wastes arising from this segment of the industry arise from the use of wet dust scrubbing equipment for the finely-divided solid products, and from such processes which use excess process water which may become a waste stream.

3.3.1 Sodium Tripolyphosphate Manufacture

Exemplary plants have no process wastes.[16,19,21] The dust collected from the spray dryer gaseous effluent stream is added to the spray dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray-dryer vent line upstream of the scrubbing operation.(19)

The neutralization step requires a total of 1,040 l/kkg (250 gal/ton), of which 290 l/kkg (70 gal/ton) are recycled from the scrubber. Make-up water, 750 l/kkg (180 gal/ton), are added since water is evaporated in the product drying step. The makup water is softened, and regeneration of the softener combined with boiler and cooling tower blowdowns amounts to 210 l/kkg (50 gal/ton); 70 per cent of which is from water treatment regeneration and 30 per cent from blowdowns. These blowdown wastes typically contain 1,500 ppm of dissolved chlorides.(19)

3.3.2 Calcium Phosphates

The raw aqueous wastes from the manufacture of food-grade calcium phosphates are from two primary and approximately equal sources: the centrate or filtrate from dewatering of the dicalcium phosphate slurry, and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely divided calcium phosphate solids. It is normal practice in an integrated plant to partially recycle the scrubber water and to partially utilize the DCP centrate or filtrate as makeup scrubber water.(15) The total raw wastes from this system are typically 4,200 l/kkg (1,000 gal/ton) containing 100 kg/kkg (200 lbs/ton) of solids (a concentration of 2.4 per cent).(15) An additional 30 kg/kkg (60 lbs/ton) of dissolved solids (0.7 per cent of this waste stream) originates from phosphoric acid mists in the scrubbers and from excess phosphoric acid in the reaction liquid.

For non-food grade dicalcium phosphate plants, the water scrubbers

which collect airborne solids normally operate at partial recycle.[25] Since there is no waste from a dewatering operation, and since dry dust collection typically precedes wet scrubbing, the raw wastes are considerably smaller than for the food-grade operation. Dry dust collection is typical since only one or two products are made, so that the collected solids may be added directly to the product stream without extensive segregation. Moreover, since purity requirements are considerably less severe, the product stream can tolerate such additions. With the above measures, the wet scrubber wastes are typically 420 l/kkg (100 gal/ton) containing 22.5 kg/kkg (45 lbs/ton) of suspended solids (a concentration of 5 per cent) plus 4 kg/kkg (8 lbs/ton) of dissolved phosphates from acid mists (0.7 per cent).[25] At the exemplary plant, this bleed stream from the wet scrubber recirculation system is charged directly to the neutralization reactor; hence, this plant had no discharge whatever.[25] As an added feature, this exemplary plant used cooling-water blowdown as makeup to the airborne-solids scrubbing system, thereby eliminating all aqueous discharges (except for the effluent from regeneration of the water softener).[25]

For the non-food grade plants, however, acid defluorination is an additional source of raw wastes (unless already-defluorinated acid is delivered to the plant). Wet-process phosphoric acid (54 per cent P_2O_5 contains approximately one per cent fluorine.[4,25] Upon silica treatment, 13.5 kg/kkg of acid (27 lbs/ton), or 10.5 kg/kkg of silicon tetrafluoride product dicalcium phosphate dihydrate (21 lbs/ton) are liberated. When hydrolyzed in the acid scrubber, the raw waste contains 12 kg/kkg product (24 lbs/ton) of combined fluosilicic acid (H_2SiF_6), hydrofluoric acid (HF) and silicic acid (H_2SiO_3). These raw wastes are contained in a scrubber water flow of 6,300 l/kkg (1,500 gal/ton), so that the combined concentration of fluosilicic acid, hydrofluoric acid and silicic acid is 1,900 ppm.[25]

For any plant manufacturing calcium phosphates of any grade, non-contact cooling water is used in reactors and/or in dried product coolers.

Other possible sources of aqueous wastes are from regeneration of water softeners and from storm water runoff (all exterior surfaces of calcium phosphate plants[15,25] become coated with fine lime and/or phosphate dusts).

In dry-product plants, a significant housecleaning effort must be continually maintained. In non-food grade calcium phosphate plants, the dry product sweepings (from dust, spills, etc) are added to the process stream.[25] In food-grade plants, however, the sweepings (consisting of lime, lime grit, and calcium phosphates) are wasted. Typically, this solid waste amounts to 10 kg/kkg (20 lbs/ton).[15]

TABLE 7

Summary of Raw Wastes from Phosphate Plants

	Sodium Tripoly-Phosphate	Food Grade Calcium Phosphates		Animal Feed Calcium Phosphates	
		Dewatering	Solids Scrubbing	Acid Defluori-nation	Solids Scrubbing
Process Water Wasted:					
l/kkg Pdt	0	2,100	2,100	6,300	420
gal/ton Pdt	0	500	500	1,500	100
Raw Waste Load, kg/kkg Pdt:					
TSS	-	50	50	-	22.5
Dissolved PO_4	-	15	15	-	4
HF, H_2SiF_6, H_2SiO_3	-	-	-	12	-
Raw Waste Load, lbs/ton Pdt:					
TSS	-	100	100	-	45
Dissolved PO_4	-	30	30	-	8
HF, H_2SiF_6, H_2SiO_3	-	-	-	24	-
Concentrations, ppm:					
TSS	-	24,000	24,000	-	54,000
Dissolved PO_4	-	7,000	7,000	-	7,000
HF, H_2SiF_6, H_2SiO_3	-	-	-	1,900	-
TDS, ppm	-	7,000	7,000	1,900	7,000
Solid Wastes: kg/kkg Pdt	0	10		-	-
lbs/ton Pdt	0	20		-	-

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4.0 The Character of Day-to-Day Effluent Data

To convey the clearest possible picture of the character of effluent data, three different parameters recorded daily for a year by Plant 159 are presented in Figures 13 through 18. These Figures have been arranged in a dual format, as follows:

a) Value of the parameter vs. time
b) Percentage frequency vs. value of the parameter (histogram).

The "spiky" appearance of the time plots is immediately apparent for all three parameters: phosphate concentration in the effluent, total phosphate discharged daily (derived from concentration and flowrate measurements), and pH. Of more significance than the "spiky" appearance is the magnitude of the variations. In Figure 15, the total phosphate discharged varies over a 5-fold range, from a minimum of 75 to a maximum of 374.

Another way to handle these data are to calculate conventional statistics:

Figures	Parameter	Mean	Standard Deviation	95% Conf. Int. for the Mean	95% Conf. Int. for a Single Day
13,14	Concentration	23.4	3.4	$\pm$ 0.4	$\pm$ 6.8
15,16	Total Discharge	234	55	$\pm$ 6	$\pm$ 110
17,18	pH	8.4	0.2	$\pm$ 0.02	$\pm$ 0.4

The last two columns would imply (for example) that the mean for total daily discharge is 95% certain to lie between 228 and 240, and that any single daily reading is 95% certain to lie between 124 and 344. An inspection of the histogram for total daily discharge (figure 16) reveals that despite the spikyness of the data, approximately 50 per cent of the readings lie above and 50 per cent lie below the mean, and approximately 95 per cent of the readings lie within the calculated confidence interval for daily readings. The other two histograms, Figures 14 and 18, reveal much the same story; that in fact conventional (Gaussian) statistics may be used with some validity despite the large excursions of the day-to-day data.

These Gaussian statistics must be treated most carefully, however, and specific conclusions must be cautiously constructed, since little is known of the cause of the large daily excursions. In analyzing data from other inorganic chemical plants (outside of the phosphorus chemicals industry), the characteristic spikyness and large daily excursions were repeated, but in some cases the histograms revealed highly non-Gaussian data distributions. In those cases, the calculated mean and standard deviation had little meaning and could only lead to misdirected effort and expense, and in extreme cases, to unrealistic decisions.

Figures 17 and 18 show that pH is much more closely controlled than either concentration or total daily discharge (the integral of concentration times flowrate). This good control of pH is understandable in physical terms, and is a characteristic commonly found during this study effort at many plants.

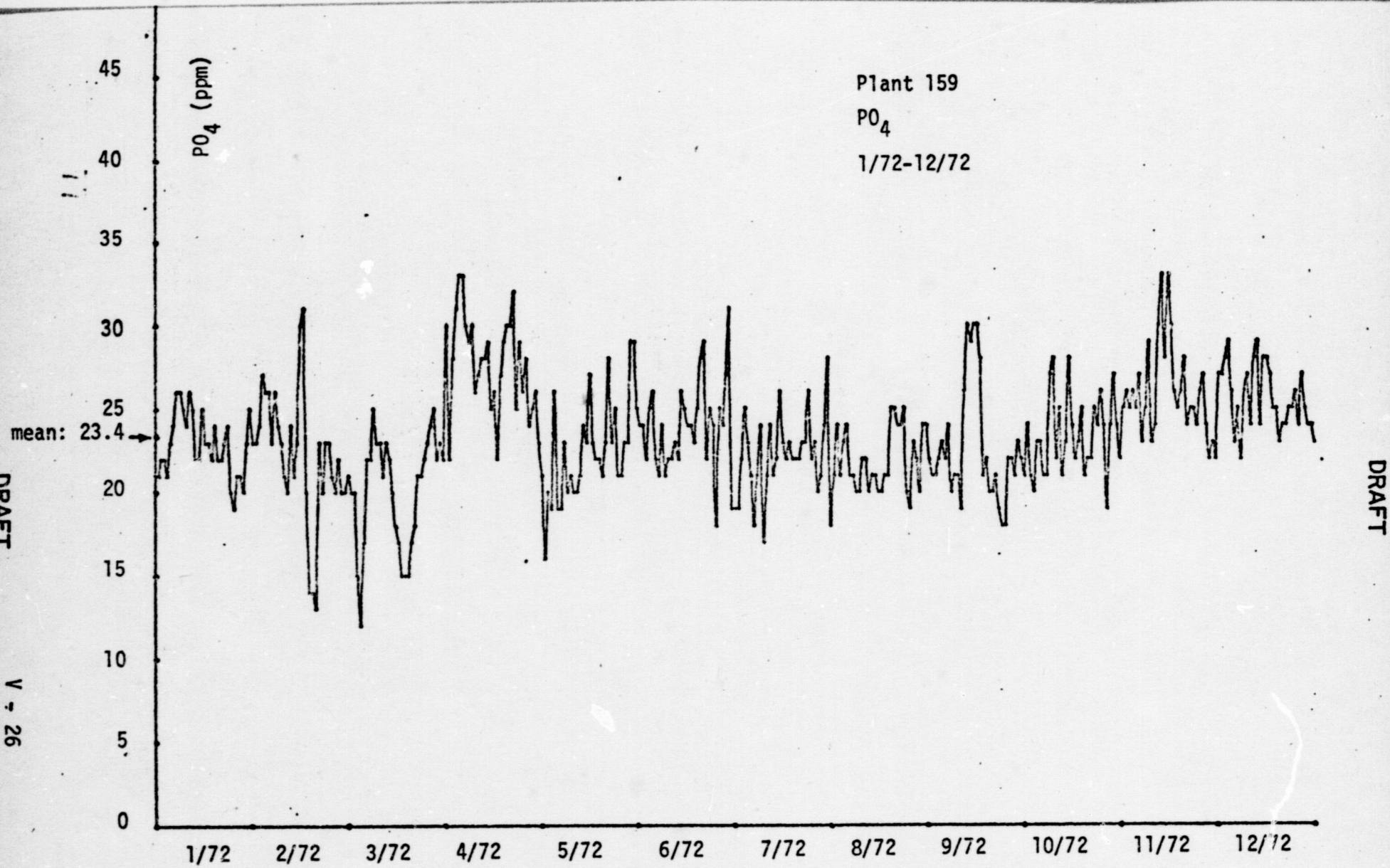

Figure 13. Phosphate Concentration vs. Time

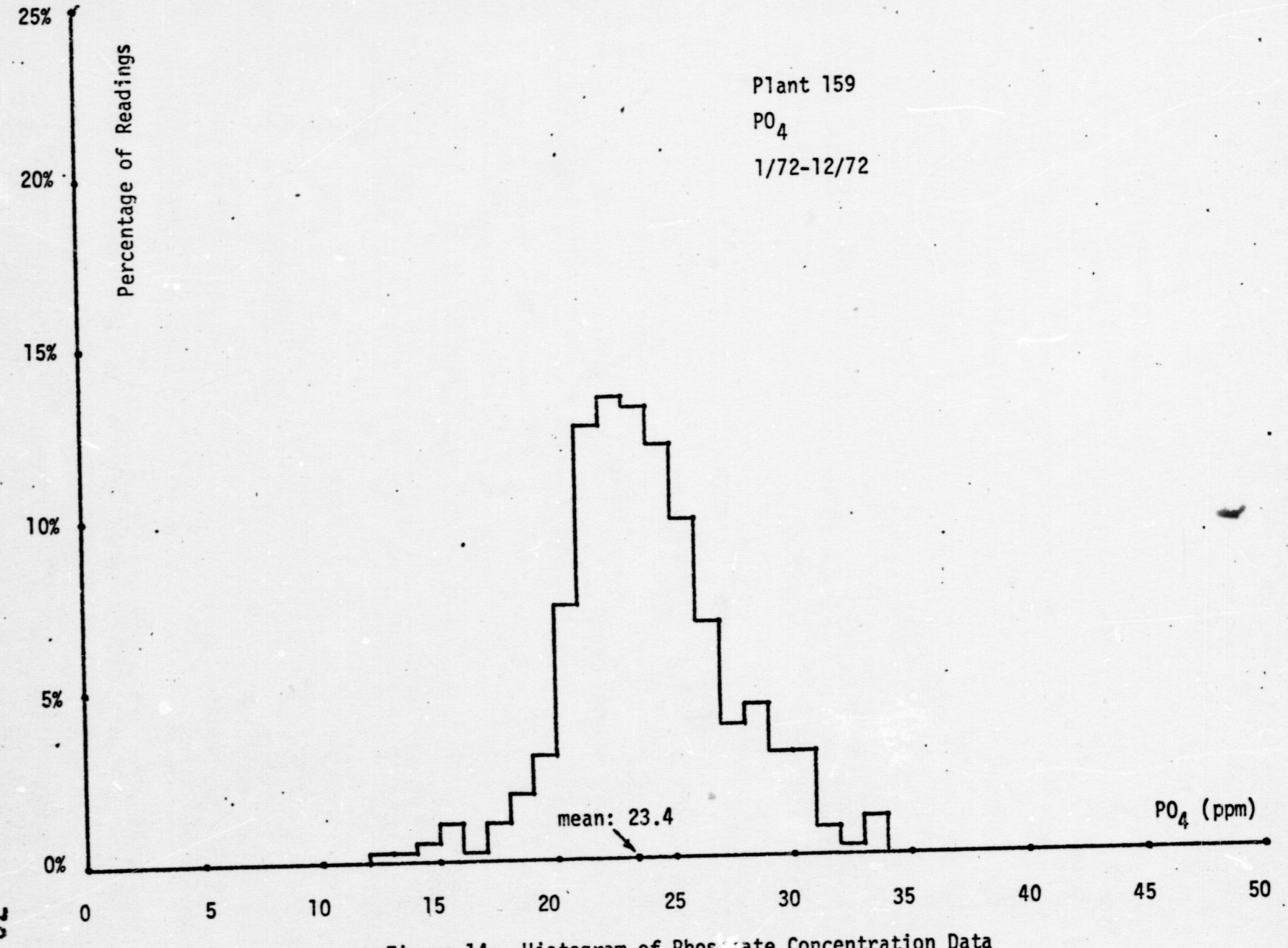

Figure 14. Histogram of Phosphate Concentration Data

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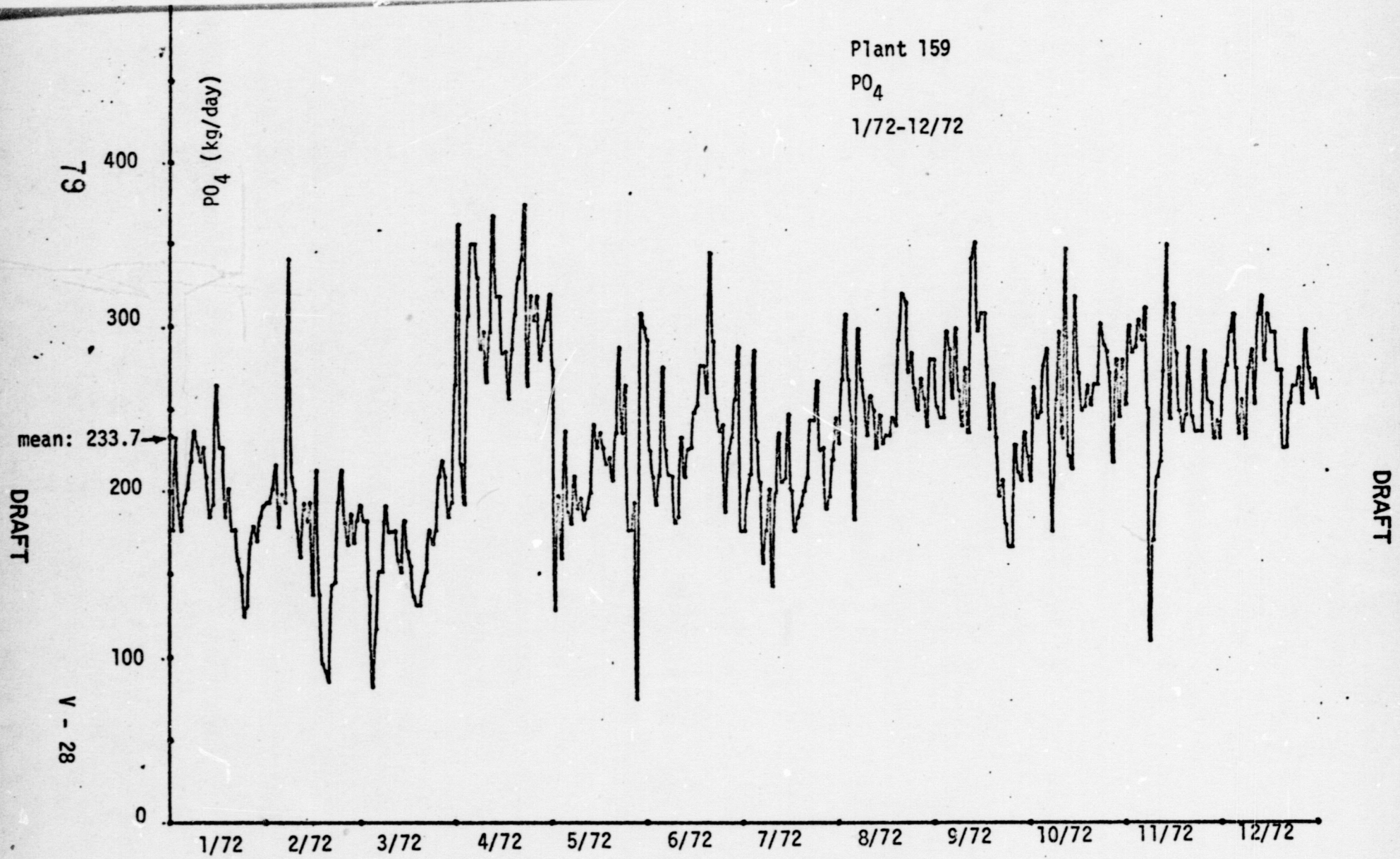

Figure 15. Total Daily Phosphate vs. Time

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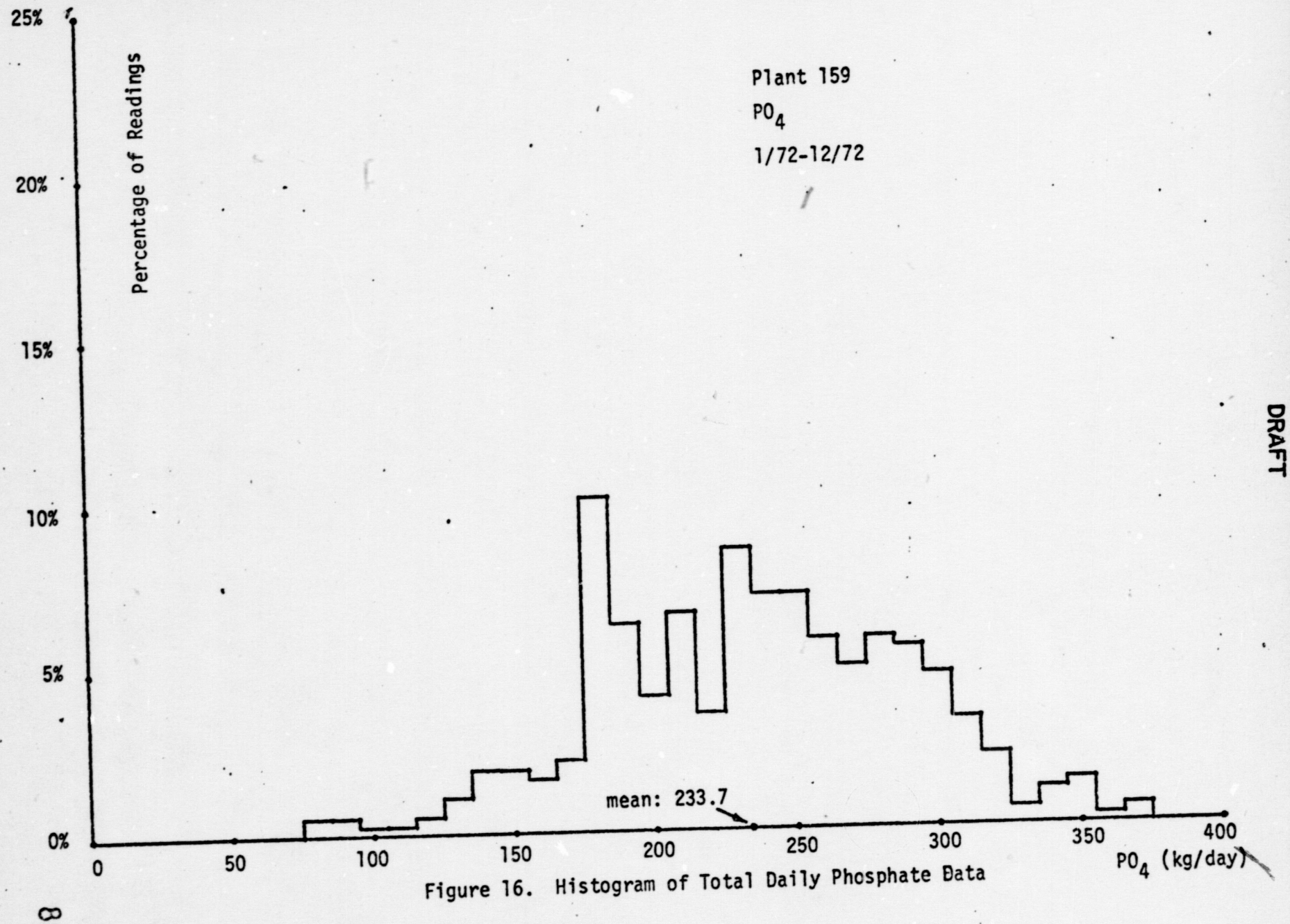

Figure 16. Histogram of Total Daily Phosphate Data

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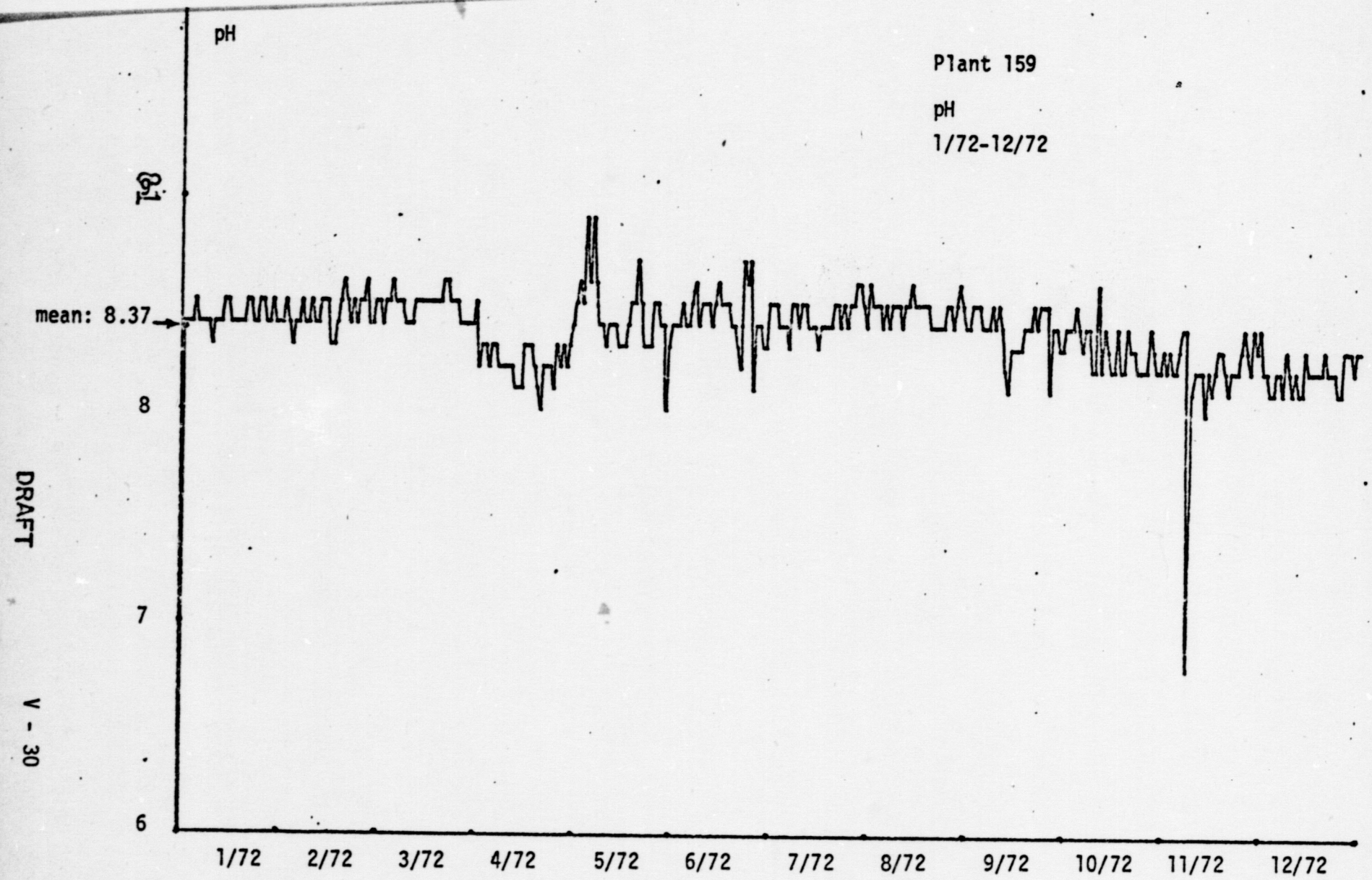

Figure 17. pH vs. Time

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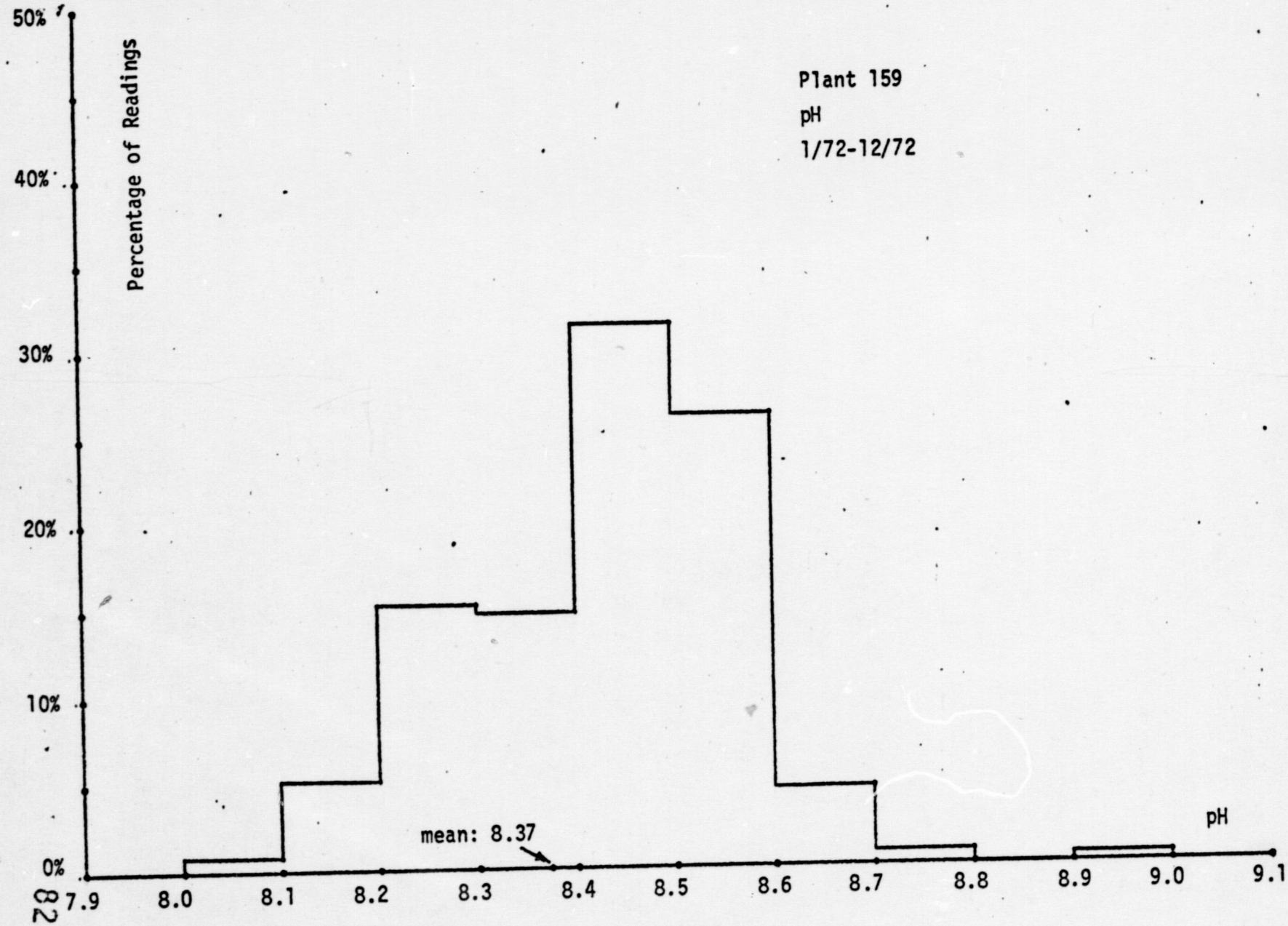

Figure 18. Histogram of pH Data

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The above data from Plant 159 represented the overflow (effluent) from a large settling pond. It is understandable, then, why pH (and to a lesser extent concentration) appears much better controlled than the flowrate-influenced total daily discharge parameter. The effluent flowrate would be much more closely coupled with the manufacturing process than the other two parameters, which are damped by the large capacity of the settling pond.

Another set of data (not as extensive, unfortunately) was obtained from Plant 037:

Date (1973)	$CaCO_3$ Acidity, ppm	Chloride, ppm
2/27	1170	560
2/28	1220	603
3/1	1720	822
4/19	850	447
4/23	480	305
4/24	950	532
4/25	1430	851
4/26	1250	589
4/27	1300	1035
4/30	1120	518
5/1	1470	1040
5/2	1690	716
5/3	280	773
5/4	1340	603
5/7	1810	1000
5/8	1220	574
5/9	1290	716
Mean	1217	687
Std, Dev.	384	208
95% Conf. Int. (Single Day)	± 814	± 441

In this case, there was no damping capacity; the acidity and chloride concentrations were closely coupled to the manufacturing process. While insufficient data was available to show a meaningful histogram, the comparison of the 95% confidence intervals with the daily data show only one point of 17 (for acidity), and no points outside (for chloride); a not surprising result.

Based on these very limited samples of data, it appears that the classical statistics may be applied, but with extreme caution.

For the above sets of data from Plants 159 and 037, a value of $(\bar{X} + 3\sigma)/\bar{X}$ might represent a maximum allowable daily reading as a multiple of the mean:

Plant	Data	$(\bar{X} + 3\sigma)/\bar{X}$
159	PO_4 Concentration	1.44
	PO_4 Daily Discharge	1.71
	pH	1.07
037	Acidity Concentration	1.95
	Chloride Concentration	1.91

This maximum allowable value would be extremely liberal, since a Students"t" value of 3 is equivalent to less than one reading in 1,000 being unduly rejected. To be even more liberal (since the data base for this analysis is extremely skimpy), the maximum value from the above table will be assumed, so that the effluent limitation guideline should be a maximum daily value no greater than twice the mean (as represented by monthly averages).

From the above discussion and data, it is apparent that pH can be controlled much more closely than other parameters. Hence, it is recommended that the daily pH limitation be the same as the corresponding monthly average limitation.

SECTION VI

SELECTION OF POLLUTION PARAMETERS

1.0 INTRODUCTION

Section V of this report quantitatively discussed the raw wastes generated in the non-fertilizer phosphorus chemicals industry. The following were identified as being constituents of the industry's process wastewaters:

Suspended Inorganic Solids
Dissolved Phosphates or Phosphites
Dissolved Sulfates or Sulfites
Dissolved Fluorides or Fluorosilicates
Dissolved Chlorides
Total Dissolved Solids
Acidity or low pH
Heat (High Temperature)
Elemental Phosphorus
Arsenic Compounds

The following discussion examines each of the above constituents and their impact upon receiving waterways from a chemical, a physical and a biological viewpoint. Additional constituents such as hexavalent chromium, iron, alkalinity, and hardness, which are of typical concern whenever blowdowns from cooling towers, boilers and water treatment facilities are involved, are noted here but are not discussed in detail in this study (which deals more specifically with the process wastes of the non-fertilizer phosphorus chemicals industry).

2.0 SUSPENDED INORGANIC SOLIDS

Suspended solids discharged into receiving waters adversely impair navigation, recreation, water supply and fish propagation water uses. Navigation may be impaired as a result of sedimentation in quiescent regions in the stream bed. Recreational and water supply uses would be impaired as a result of turbidity of the water. The fish population suffers from loss of suitable breeding areas, loss of food chain organisms because of change in benthic characteristics, fish kills from excessive turbidity, and reduction of light penetration into the stream.

Suspended solids affect fisheries directly by covering the bottom of a stream with a blanket of material which kills out the bottom fauna, directly depriving the fish of a considerable part of their food (which lies at the bottom),

or indirectly by eliminating species in the food chain. In addition, portions of the bottom usually in the shallower parts of the stream provide nesting sites and spawning grounds for certain species.

The suspended solids directly affect fish through mechanical and abrasive action which clogs or otherwise injures the gills and respiratory structures. Although normal healthy fish secrete mucus to wash away suspended solids as they lodge on gills and other exposed parts, the synergistic action of other pollutants such as small amounts of acid wastes greatly augments the abrasion by solids by inhibiting the normal flow of mucus.(44)

Indirectly, suspended solids affect fisheries by effectively screening out the light necessary to species of flora which may be important parts of the food chain. Also indirectly, but none the less effectively, solids which settle at the bottom trap organic wastes which might otherwise be dispersed, thereby increasing the oxygen demand at the bottom of the stream with disastrous results to the bottom fauna.(44)

Of special concern in the non-fertilizer phosphorus chemicals industry is that much of the suspended solids in the raw wastes are calcium phosphates. It has recently been shown that calcium phosphates deposited in bottom muds of lakes are not inert solids, but are indeed available for uptake by the lake waters, and are a prime source of nutrients for algae blooms and a prime cause for lake eutrophication.(46)

3.0 DISSOLVED PHOSPHATES AND PHOSPHITES

Phosphites are oxidized to phosphates in streams, exerting a chemical oxygen demand upon the streams.

The controversy over the nutrient and eutrophication effects of phosphates have received much attention in recent years, resulting from the phosphate constituent in domestic wastewater. The average concentration in domestic wastewater is 30 ppm (as PO_4); and the domestic waste quantities are about 1.6 Kg (3.5 lbs) per capita per year, one-third of which are from human excretions and two-thirds from synthetic detergents.(31) Runoff of synthetic fertilizers also contribute heavily to phosphate pollution of surface waters.

Eutrophication, the nutrient enrichment of water resulting in excessive growth ("blooms") of algae and aquatic weeds, is a natural slow process generally referred to as the natural aging of lakes. This process has been enhanced by man's introduction of nutrients such as phosphates from industrial, municipal and agricultural wastes. The excessive growth of algae are unsightly, interfere with the recreational use of the water, contribute unpleasant tastes and odors to the water, and when the algae die and putrefy, they consume the dissolved oxygen in the water thereby killing fish and other aquatic animal life.(46)

The cause-and-effect relationship between phosphates and eutrophication is not altogether proven, and has been the subject of much research and controversy.(34,45) For the purposes of this study, it appears sufficient to rely for guidance upon the massive effort and expenditure to remove phosphates from domestic wastewater; in order to come to the conclusion that dissolved phosphates from the industry under study are indeed a pollution parameter.

The natural concentration of phosphates in sea water is 0.7 to 1.4 ppm.(49)

4.0 DISSOLVED SULFATES OR SULFITES

Sulfites are oxidized to sulfates in streams, exerting a chemical oxygen demand upon the streams. They are also toxic to fish; 100 ppm of sodium sulfite in hard water killed goldfish in 96 hours, and 1,000 ppm killed goldfish in 3 to 72 hours.(44) Sulfur dioxide at 10 ppm in tap water caused trout to float helplessly in 10 minutes, and at 16 to 19 ppm killed orange-spotted sunfish in one hour.(44)

Sulfates are not particularly toxic, but are a major constituent of the total dissolved solids in wastewaters from this industry (and are discussed separately as such).

5.0 DISSOLVED FLUORIDES AND FLUOROSILICATES

Fluosilicic acid and its salts are highly toxic materials.(48) They also decompose to form fluorides.

Fluorides are present in natural waters in concentrations less than 1 ppm, and are widely used as drinking water additives in concentrations of a few ppm for beneficial dental effects. However, at higher concentrations than 7 or 8 ppm, fluorides have caused severe damage to bone structures. Fluorosis from airborne fluorides has been documented in cattle and in humans in the proximity of phosphate-rock mining operations, and a maximum concentration of total fluoride in air of 2.5 mg/m^3 has been recommended.(48)

Fluorides and fluorosilicates are definitely toxic materials, and can be identified as pollution parameters for the purposes of this study.

6.0 DISSOLVED CHLORIDES

Dissolved chlorides are a major constituent of the total dissolved solids in wastewaters from this industry (and are discussed separately as such).

Sodium and calcium chlorides are found naturally in unpolluted waters, but are toxic to fish in high concentrations. Straw-colored minnows were killed in 2,775 ppm of $CaCl_2$ in 2 to 4 days and in 2,500 ppm of NaCl in 9 to 24 days; goldfish were killed in 7,752 ppm of $CaCl_2$ in 22 to 27 hours and in 11,765 ppm of NaCl in 17 hours; and gold shiners were killed in 5,000 ppm of $CaCl_2$ in 143 hours and in 5,000 ppm of NaCl in 148 hours.(44)

Some common estuarine-dependent plants and animals have well-defined salinity ranges:(49)

Species	Salinity range, ppm Cl^-
Atlantic Oyster	7,000 - 27,000
Oyster Drill	15,000 - 28,000
Blue Crab	0 - 34,000
Adult Shrimp	33,000 - 37,000
Turtle Grass	25,000 - 40,000
Salt Marsh Grass	15,000 - 40,000

The natural salinity of river water in the Chesapeake Estuary is 9.5 to 11.0 ppm of chloride; and the natural salinity of ocean water is 7,000 to 10,300 ppm of chloride.(49)

7.0 TOTAL DISSOLVED SOLIDS

Unpolluted natural waters contain small quantities of dissolved carbonates, chlorides, phosphates, sulfates and nitrates. All of the substances in solution in river water exert osmotic pressure on the aquatic organisms, and many of these substances are physiologically active, so that the organisms have become adapted to this salt complex. Most aquatic species will tolerate changes of considerable magnitude in the relative amounts of these salts provided the total dissolved solids remains constant.(44)

The specific conductance, a direct measure of dissolved inorganic solids, lies between 150 and 500 µmhos/cm in inland streams and rivers which support good, mixed fish faunas. In the Western plains and desert areas, natural quantities of dissolved solids are higher, with specific conductance ranging to 2,000 µmhos/cm. The blood of fresh-water fish contain approximately 7,000 ppm of dissolved salts (mainly NaCl). If the total dissolved solids in the external medium exceeds this 7,000 ppm by much, water will be withdrawn by osmosis from the gills of fish and from other delicate external organs of various species of aquatic life with lethal effects (as noted by the data in paragraph 6.0 for sodium chloride).(44)

8.0 ACIDITY OR LOW pH

Acidity, or low pH, kills fish through the precipitation and coagulation of the mucus on the gills and by the coagulation of the gill membranes themselves (specifically the proteins in the membranes). This precipitation and coagulation proceeds rapidly below a pH of 4.5; but species unprotected by mucus (such as Daphnia magna) are killed below a pH of 5.5. Representative survival data is in Table 8. (44)

A typical State water quality standard (that of Maryland) specifies a pH of 6.0 to 8.5 regardless of water use.(50)

9.0 HEAT (HIGH TEMPERATURE)

The impact of high water temperatures takes several forms which may also act synergistically:

(a) Alteration of the physical properties of water

(b) Decrease in the solubility of oxygen upon which most aquatic organisms depend.

(c) Increase in the rate of chemical and biochemical reactions, particularly in the oxidation of organic wastes (thereby decreasing the level of dissolved oxygen).

(d) At sufficiently high temperatures, organisms are killed directly.

(e) Physiological processes such as reproduction, development and metabolism are temperature-dependent.

(f) Temperature anomalies can block the passage of anadromous fish, greatly reducing future populations.

Most fish are poikilothermal animals whose body temperature follows changes in environmental temperatures rapidly and precisely. The tolerance of fish to high temperatures is dependent upon the normal temperature to which the fish are acclimated and to the abruptness of temperature changes (both temporally and spatially). In general, however, the upper temperature limits for fish survival are in the range of 25 to 35°C (75 to 95°F)(49,51)

A typical state water quality standard (that of Maryland) specifies the following with respect to heat rise regardless of water use(50):

TABLE 8. Survival of Aquatic Species in Acids
Source: Ellis[44]

Species	Acid	pH	Survival Time, Minutes
Goldfish	HCl	1.8	10-15
		3.0	75-90
		3.5	83-135
		4.0	268-392
		4.5	∞
		6.9	∞
Goldfish	H_sSO_4	2.2	30-45
		3.0	50-70
		3.5	150-317
		3.9	300-360
		5.0	∞
		6.8	∞
Daphnia Magna	HCl	4.0	60-240
		5.0	240-1,020
		5.4	1,020-4,320
Daphnia Magna	H_2SO_4	3.5	60-180
		4.0	1,440
		5.0	1,440-4,320

Type of Water	Natural Temp,°F	Max.Temp Rise,°F	Maximum Temp,°F
Tidal	< 50 < 50	20 10	60 90
Non-Tidal	< 50 < 50	20 10	60 93

10.0 ELEMENTAL PHOSPHORUS

Elemental phosphorus has been identified as an extremely toxic material in very small amounts.(5) The lethal dose for humans is 100 mg and the chronic dose is 1 mg/day. Ingestion of elemental phosphorus by the human body causes bone and liver damage.

Goldfish minnows died upon exposure to water containing 0.10 ppm of phosphorus in 48 hours, and to water containing 0.05 ppm in 163 hours.(5) The effect of phosphorus upon lobsters has been studied.(154)

11.0 ARSENIC COMPOUNDS

The toxicity of arsenic compounds in very small amounts is well known. The Federal Water Quality Administration presented a summary of the hazards of arsenic.(47) The U. S. Public Health Service Drinking Water Standards set a maximum concentration of 0.05 ppm, with a recommended limit of 0.01 ppm.(53) There is a continuing controversy over the health hazards of minute quantities of arsenic either naturally entering the ground or surface waters; and particularly over the arsenic that occurs naturally in phosphates (at a level of As:P of 75 ppm) and is subsequently discharged into municipal wastewater.(47,52,53,55,56,57)

12.0 CONCLUSION

In view of the data presented above, it is judged that all of the mentioned waste constituents generated in the non-fertilizer phosphorus chemicals industry be identified as pollution parameters as defined in the Federal Water Pollution Control Act Amendments of 1972.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

1.0 INTRODUCTION

Section V of this report quantitatively discussed the specific water uses in the non-fertilizer phosphorus chemicals industry and the raw wastes from this industry prior to control and/or treatment of these wastes. Section VI identified the constituents of the raw wastes which are classified as pollutants. The following table summarizes the pollutant constituents found as raw wastes in each of the three segments of the industry:

	Phosphorus Production	Phosphorus Consumption	Phosphates
Suspended Inorganic Solids	X		X
Elemental Phosphorus	X	X	X
Dissolved Phosphates or Phosphites	X	X	X
Dissolved Sulfates or Sulfites	X	X	
Dissolved Fluorides or Fluorosilicates	X		X
Dissolved Chlorides		X	
Arsenic Compounds*	X	X	
Acidity	X	X	X
Heat	X	X	X

*Concentrated, in excess of natural proportion in phosphorus compounds

Two major observations may be made from the above table:

1. Classical sanitary engineering practices that treat effluents containing organic material or that are aimed at reducing biological oxygen demand are inapplicable to the phosphorus chemicals industry, where such pollutant constituents are usually very low and not a significant factor. Hence, control and treatment of the wastes in this industry are of the chemical and chemical engineering variety, and include neutralization, pH control,

precipitation, ionic reactions, filtration, centrifugation, ion exchange, demineralization, evaporation and drying.

2. A limited number of pollutant constituents characterizes the entire industry, crossing the lines between segments of the industry. Hence, the control and treatment techniques should be similar throughout the industry.

In this section of the report, the control and treatment technoloty is discussed in considerable detail. Much of this discussion is based upon observed actual abatement practice in the industry; the accomplishments of exemplary plants are specifically noted and are quantitatively supported by independently-verified sampling data of plant effluents. There were many instances, during this study of exemplary plants, of conscientious and successful waste abatement programs. Profitable waste segregations and recoveries, closed cycles, leak and spill containments, and in-process waste reductions are commonplace. Some of these waste abatement programs have not involved much money, but most have been expensive.

Discharge of acidic or alkaline wastes to surface water is uncommon and is becoming more so all the time. Toxic wastes such as phosphorus and arsenic are being removed with increasing efficiency. Technology has been developed for removal of these toxic materials to very low levels. In exemplary plants, specified or acceptable water quality levels are being met. Public outcry and/or consensus agreement on the need to clean up these toxic wastes has resulted in positive and effective action on the part of industry.

Because the waste control and treatment challenges cross the lines between segments of the industry, the following discussion is organized according to the treatment methods and the types of raw wastes to be treated. In Section IX, Best Practicable Control Technology Currently Available, the industry is discussed on a chemical-by-chemical basis with verified effluent data presented where applicable.

2.0 IN-PROCESS CONTROLS

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices.

2.1 Segregation of Water Streams

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

Incoming pure water picks up contaminants from various uses and sources including:

1. non-contact cooling water
2. contact cooling water

3. process water
4. washings, leaks and spills
5. incoming water treatments
6. cooling tower blowdowns
7. boiler blowdowns

If wastes from these sources are segregated logically, their treatment and disposal may sometimes be eliminated entirely through use in other processes or recycle. In many instances, the treatment costs, complexity and energy requirements may be significantly reduced. Unfortunately, it is a common practice today to blend small, heavily contaminated streams into large non-contaminated streams such as cooling water effluents. Once this has been allowed to happen, treatment costs, energy requirements for these treatments, and the efficient use of water resources have all been compromised.

In general, plant effluents can be segregated into:

1. Non-contaminated Cooling Water. Except for leaks, non-contact water has no waste pickup. It is usually high volume.

2. Process Water. Usually contaminated but often small volume.

3. Auxiliary Streams. Ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks, washings - low volume but often highly contaminated.

Although situations vary, the basic segregation principle is don't mix large uncontaminated cooling water streams with a smaller contaminated process and auxiliary streams prior to full treatment and/or disposal. It is almost always easier and more economical to treat and dispose of the small volumes of waste effluents - capital costs, energy requirements, and operating costs are all lower.

In the phosphorus chemicals industry, many plants have accomplished the desired segregation of water streams, often by a painstaking rerouting of sewer lines which have existed for many years. Among those plants which are exemplary in this respect are Plants 003, 037, 042, 075, and 182.

2.2 Recycle of Scrubber Water

The widespread use of water for scrubbing of tail gases in this industry has unfortunately led to many examples where once-through scrubber water is the mode of operation. However, there are several plants exemplary in this respect which recycle scrubber water from a sump, thus satisfying the scrubber water flowrate demands (based upon mass transfer considerations) while retaining control of water usage. These exemplary plants are TVA (Muscle Shoals, Alabama)[5,7], and Plants 003 and 182.

Recycle of scrubber water permits the subsequent treatment of much smaller quantities of wastewater with much higher concentrations of polluting constituents. Both of these attributes make wastewater treatment more economical, and in some cases, more efficient, from a removal viewpoint.

2.3 Dry Dust Collection

A drastic reduction in the aqueous waste load may be made by replacing wet scrubbing systems with baghouses, or alternately, by placing cyclone dust collectors upstream of wet scrubbers. This approach is feasible because baghouses have recently been improved in design to the point where operation and maintenance costs are not excessive, where solids collection efficiencies exceed those of wet scrubbers, and where operating temperature ranges have been extended with high-temperature media development. Dry collected solids may be returned to the product stream, provided that a separate collector is installed for each product. This is a change in approach for the typical multi-product phosphate plant, since conventional practice has been to centralize the collection and treatment functions across product lines. With dry separate collection, the product recovered may significantly contribute towards the operating cost of the collectors.

Plants in this industry which are exemplary in this respect by having at least some dry dust collection include Plants 003, 006, 042, 119, and 182.

2.4 Refrigerated Condensers for PCl_3 and $POCl_3$

In the standard processes for manufacturing PCl_3 and $POCl_3$, the present industry practice is to use water-cooled condensers to reflux the reaction vapors and to collect the product. Because the vapor pressure of PCl_3 is significantly high (boiling point 76°C (169°F) at normal condensing temperatures, the raw waste load in the tail-gas water scrubbers contain rather large quantities of the hydrolysis products of PCl_3.

The use of refrigerated condensers in place of the water-cooled condensers; or alternately, the use of cold traps downstream of the water-cooled condensers; would drastically reduce the amount of PCl_3 in the tail gas which subsequently becomes acid aqueous wastes:

Temperature, °C	Temperature, °F	PCl_3 Vapor Pressure, mm Hg(27)
-40	-40	3
-20	- 4	13
0	32	38
+20	68	99
+40	104	235

95

It is apparent that a condensing temperature below -20°C (-4°F) would lower the PCl_3 vapor pressure by an order of magnitude over normal condensing temperatures, and would virtually double the temperature driving force for heat transfer.

Refrigerated condensers are in current use (for $POCl_3$ manufacture using air oxidation) at Plant 037.

2.5 Inert-Atmosphere Casting of P_2S_5

The present industry practice is to cast molten P_2S_5 product into shipping containers or into conical forms. When molten P_2S_5 is exposed to the atmosphere, it spontaneously ignites, forming P_2O_5 and SO_2 which are subsequently water-scrubbed.

There are various state-of-the-art techniques available for casting either in an inert atmosphere or in vacuum, to eliminate this source of raw aqueous waste.

2.6 Housekeeping and Containment

Containment and disposal requirements may be divided into several categories:

1. minor product spills and leaks
2. major product spills and leaks
3. upsets and disposal failures
4. storm water runoff
5. pond failures
6. vessel and container cleanout

2.6.1 Minor Spills and Leaks

There are minor spills and leaks in all industrial chemical manufacturing operations. Pumps seals leak, hoses drip, washdowns of equipment, pipes and equipment leak, valves drip, tank leaks occur, solids spill and so on. These are not going to be eliminated. They can be minimized and contained. In some cases the products are valuable; in other cases, personnel safety and prevention of corrosion may become paramount.

Reduction techniques are mainly good housekeeping and attention to sound engineering and maintenance practices. Pump seals or type of pumps are changed. Valves are selected for minimizing drips. Pipe and equipment leaks are minimized by selection of corrosion-resistant materials.

Containment techniques include drip pans under pumps, valves, critical small tanks or equipment, and known leak and drip areas such as loading or unloading stations. Solids can be cleaned up or washed down. All of these minor leaks and spills should then go to a containment system, catch basin, sump pump or other area that collects and isolates all of them from other water systems. They should go from this system to suitable treatment facilities.

Of special importance in the phosphorus-consuming segment of the industry is the containment of phossy water from phosphorus transfer and storage operations. While displaced phossy water is nominally shipped back to the phosphorus-producing facility, current practice in phosphorus storage tanks is to maintain a water blanket for safety reasons by makeup water addition and by subsequent overflow over a weir of excess water.

This method of level control is unacceptable since it results in the discharge of phossy water. One way to ensure zero discharge is to install an auxiliary tank to collect phossy water overflows from the phosphorus storage tank; this system can be closed-loop by reusing this phossy water from the auxiliary tank as makeup for the main phosphorus tank. This scheme preserves the positive safety features of the existing level control practice and also safeguards against inadvertently large discharges resulting from leaky or maladjusted water makeup valves.

2.6.2 Major Product Spills and Leaks

These are catastrophic occurrences with major loss of product -- tank and pipe ruptures, open valves, explosives, fires, earthquakes.

No one can predict, plan for or totally avoid these happenings; but they are extremely rare. Probably the most common of these rare occurrences is tank or valve failures. These can be handled by adequate dikes able to contain the tank volume. All acid, caustic or toxic material tanks should be diked to provide this protection. Other special precautions may be needed for flammable or explosive substances. Plant 037 is a prime example where product tanks and transfer pumps have been systematically diked for containment or spills.

2.6.3 Upsets and Disposal Failures

In many processes there are short term upsets. These may occur during start-up, shutdown or during normal operation. The phosphorus-consuming segment and the phosphate segment of this industry may be more vulnerable to this type of upset since so many of the processes are batch-type operations with much more direct operator control than the typical large-scale automated continuous processes in the chemical industry.

These upsets represent a small portion of overall production but they nevertheless contribute to waste loads. Hopefully, the upset products may be treated, separated, and largely recycled. In the event that this can not be

done, they must be disposed of.

One very special problem in the phosphorus-consuming segment is the inadvertent spill of elemental phosphorus into a plant sewer line. Past practice has been to let it remain in the sewer and to ensure a continuous water flow to prevent fire. There has been general reluctance to clean it out since phosphorus burns when exposed to air. With this practice, of course, all water flowing in that sewer from that time on contacts phosphorus and ostensibly becomes contaminated.

Provisions can be made for collecting, segregating and bypassing such phosphorus spills. One method is the installation of a trap of sufficient volume just downstream of reaction vessels, with appropriate installations and valving to enable the bypass of that trap after a spill has occurred and the off-line removal and cleaning of the trap (with safe disposal of the phosphorus).

2.6.4 Stormwater Runoff

The phosphates segment of this industry is characterized by the handling, storing, conveying, sizing, packaging and shipping of finely-divided solid products. Typically, a phosphates plant has all exterior surface of buildings, equipment and grounds covered with dusts. An area of concern is the pickup of these solids by stormwater either as suspended solids or as dissolved solids. Of course, washing down of these dusts is not acceptable; the dry solids must be collected. Where possible, the solids may be returned to appropriate process streams. Where purity requirements prohibit this return, adequate means for safe disposal of solid wastes must be provided.

Plants 003, 042 and 182 are examples of plants which have positive continual cleanup programs for solids, which minimize stormwater runoff. Most plants (with considerable credit to air pollution abatement practices) have also minimized the quantity of airborne dusts.

The very practice of process water segregation discussed in Section 2.1 has led to the direct discharge of stormwater without treatment. Little is known from a quantitative standpoint about the severity of this problem in the phosphates segment of the industry, or to what extent containment and treatment of stormwater is required. In the phosphorus manufacturing segment of the industry, where large quantities of dusts are handled, Plant 159 collects approximately 10 kg/kkg (20 lbs/ton) in a settling pond for stormwater and non-contact cooling water.

2.6.5 Pond Failures

Unlined ponds are the most common treatment facility used by the industry. Failures of such ponds occur because they are unlined and because they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control if dug in impervious clay areas

or poor control if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. This may or may not be detrimental to the area, but it is certainly poor waste control. Lined ponds are the only answer in these circumstances.

Many ponds used today are large low-diked basins. In times of heavy rainfall, much of the pond content is released into either the surrounding countryside, or, more likely, into the nearest body of water. Again, whether this discharge is harmful or not depends on the effluent and the surrounding area, but it does represent poor effluent control.

Good effluent control may be gained by a number of methods, including:

1. Pond and diking should be designed to take the anticipated rainfall - smaller and deeper ponds should be used where feasible.

2. Control ponds should be constructed so that drainage from the surrounding area does not innundate the pond and overwhelm it.

3. Substitution of smaller volume (and surfaced) treatment tanks, coagulators or clarifiers can reduce rainfall influx and leakage problems.

2.6.6 Vessel and Container Cleanout

One common characteristic of the phosphorus-consuming segment of the industry is the planned accumulation of residues in reaction vessels and stills, with infrequent shutdowns to clean and remove these residues. In many cases, the residues are washed down with firehoses and the wastes discharged. This practice is clearly unacceptable. One alternative is the diking of the area (as described previously), with collection and treatment of the aqueous wastes, in conjunction with an effort to minimize the quantities of washwater.

A similar situation exists with regard to the cleaning of returnable containers (drums, tank trucks and tank cars) prior to reuse. Since these are routine operations, procedures and facilities must be made available for minimizing the quantities of wastewater and for the collection and treatment of these wastewaters.

2.6.7 Monitoring Techniques

Since the chemical process industry is among the leaders in instrumentation practices and application of analytical techniques to process monitoring and control, there is rarely any problem in finding technology applicable to wastewater analysis.

Acidity and alkalinity are detected by pH meters, often installed in-line for

continuous monitoring and control.

Dissolved solids may be estimated by conductivity measurements, suspended solids and turbidity, and specific ions by wet chemistry and colorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most universal of the in-line monitoring instruments. Spills, washdowns and other contributions become quickly evident. Alarms set off by sudden pH changes alert the operations and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

Monitoring and control of toxic materials such as phosphorus and arsenic is often so critical that batch techniques may be used. Each batch can be analyzed before discharging. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. This follows from the fact that most dissolved solids are of rather low toxicity. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates, and other low ion concentrations.

3.0 TREATMENT OF SPECIFIC WASTE CONSTITUENTS

3.1 Neutralization of Acidic Wastewaters

Virtually every manufacturing process in the non-fertilizer phosphorus chemicals industry results in a raw waste load of significant acidity. In some cases, advantage is taken of the availability of alkaline waste to at least partially neutralize the acid waste streams.

At phosphorus-producing plants, some neutralization of acidic calciner scrubber liquor is achieved by the alkaline slag or by the slightly alkaline slag quench liquor (see Table 4). At TVA[7], the slag is granulated by quenching with a high-velocity jet of calciner scrubber liquor plus process cooling water; the granulated slag (with its large surface area) effectively neutralizes the acidic liquors. At plants not granulating slag, the slightly-alkaline slag quench liquors are mixed with the highly-acidic scrubber liquors for partial neutralization. This is practiced at Plants 028 and 181.

Except for this one case where granulated slag is available, lime or limestone neutralization of acid waste streams is standard practice in this industry, as observed at Plants 003, 006, 028, 159, 181, and 182. The relative chemical costs reported by Downing, Kunin and Polliot[28], listed in Table 8, show that limestone or lime are far and away more economical than other neutralizing materials. Limestone is the lower cost material (approximately

TABLE 8. Relative Chemical Costs for Neutralizing Acid Wastes
Source: Downing, Kunin and Polliot[28]

NEUTRALIZING MATERIAL	Relative Cost per Pound Alkali*	Relative Weight Alkali Required Per Pound Acid			Relative Cost Per Pound Acid		
		H_2SO_4	HCl	H_3PO_4	H_2SO_4	HCl	H_3PO_4
Lump limestone, high Ca	1.16	110	148	165	128	172	191
Lump limestone, dolomitic	1.00	94	127	141	94	127	141
Pulv. limestone, high Ca	1.59	110	148	165	175	235	262
Pulv. limestone, dolomitic	1.37	94	127	141	129	174	193
Hydrated lime, high Ca	3.06	79	107	119	242	327	364
Hydrated lime, dolomitic	2.50	65	87	98	162	217	245
Pebble lime, high Ca	2.07	60	80	90	124	166	186
Pebble lime, dolomitic	1.87	54	73	81	101	136	151
Pulv. quicklime, high Ca	2.18	60	80	90	131	174	196
Pulv. quicklime, dolomitic	1.97	54	73	81	106	144	159
Sodium bicarbonate	20.65	173	233	260	3570	4810	5360
Soda ash	13.08	119	160	179	1560	2090	2340
Caustic soda (50%)	9.96	164	220	246	1630	2190	2450
Ammonia (anhyd.)	5.90	35	47	53	207	277	313
Magnesium oxide	3.90	42	56	63	164	218	246

*Delivered cost including freight.

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$11/kkg ($10/ton)) but suffers the disadvantages of slower reaction and lower obtainable pH than with lime. Lime costs are approximately $22/kkg ($20/ton).

With the exception of hydrochloric acid from PCl_3 and $POCl_3$ manufacturing facilities, every acid waste in the phosphorus chemicals industry forms insoluble or slightly-soluble calcium salts when treated with lime:

Acid	Calcium Salt	Solubility*, ppm (27,29)
H_3PO_4	$Ca(H_2PO_4)_2 \cdot H_2O$, MCP	18,000
"	$CaHPO_4 \cdot 2H_2O$, DCP	200
"	$Ca_3(PO_4)_2$, TCP	25
HF, H_2SiF_6	CaF_2	16
H_2SiO_3	$CaSiO_3$	95
H_2SO_4	$CaSO_4 \cdot 2H_2O$	2,410
H_2SO_3	$CaSO_3 \cdot 2H_2O$	43
H_3PO_3	$2\ CaHPO_3 \cdot 3H_2O$	(Slightly Soluble)

*Between 17°C and 30°C

It is readily apparent that lime treatment (with excess lime) not only performs neutralization of acidic wastewaters from the non-fertilizer phosphorus chemicals industry, but also demineralizes most wastewaters by precipitating calcium salts.

3.2 Treatment of Arsenic-Rich Residues

Arsenic-rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. The standard disposal method is burial in a controlled area, as practiced at Plants 075, 119, 147 and 192.

The arsenic-rich liquid residue from the PCl_3 distillation is more difficult to dispose of. At Plant 037, this residue is first treated with trichloroethylene, in which PCl_3 is miscible but $AsCl_3$ is not. The trichloroethylene

is then water-washed to remove the arsenic-free PCl_3 and the trichloroethylene is reused. The $AsCl_3$-rich residue is then segregated and stored in drums for final disposal. Since the quantities involved are small and since these wastes are only infrequently generated (not continuously), they may be disposed of by a licensed commercial contractor.

3.3 Control and Treatment of Phossy Water at Phosphorus-Producing Plants

Because of the extreme toxicity of elemental phosphorus in small concentrations in wastewater, and because complete removal of the phosphorus from the water is not practical, it is universal practice at phosphorus-producing plants to reuse the phossy water after treatment (which is required to remove other constituents in the wastewater which would otherwise build up in concentration).

Barber[5] discusses several methods tried experimentally to remove elemental phosphorus from phossy water. Among these methods were chlorination, which was tried more than 20 years ago and which was discarded at that time because "accurate chlorinator control was found to be impractical". With the development of chlorine analyzer-controllers for municipal wastewater treatment, however, it appears that chlorination deserves another trial. Air-oxidation was attempted, but the reaction was far from complete, leaving 14 to 37 per cent of the original colloidal phosphorus unoxidized. Filtration of the colloidal phosphorus was investigated but found impractical. As a result of these discouraging results, the industry has adopted the route of containment and reuse rather than treatment and discharge.

At the TVA Muscle Shoals plant[5], a commercial flocculant, Magnifloc 521C, at a concentration of 40 ppm, is employed to settle both the phosphorus and the suspended solids. Using a clarifier, the system removes 92 to 93 per cent of both the phosphorus and the suspended solids as the phosphorus sludge underflow (which is only 2 per cent of the wastewater volume).

The underflow from the clarifier may be treated as other phosphorus muds or sludges are treated. The sludge may be gravity-thickened and/or dewatered by centrifugation or filtration. The sludge, thickened sludge, or sludge cake (with respectively lower moisture contents) may then be heat-dried in an inert atmosphere using the process byproduct carbon monoxide as fuel. Elemental phosphorus (nominally 40 to 65 per cent of the "solids" in the sludge) are recovered. The remaining non-volatile solids contain no elemental phosphorus and can be safely disposed of or recycled to the feed preparation section of the phosphorus manufacturing plant.

The clarifier overflow, containing only 7 or 8 per cent of the original phosphorus and suspended solids, may then be recirculated to the phosphorus condenser sump and to other areas where water contacts phosphorus. However, because the phossy water accumulates dissolved salts (mainly fluorides and phosphates, see Table 4), about 6 per cent of the clarified water must be bled off and discharged.[5] In addition to suspended solids and dissolved

solids, this bleed contains 120 ppm of elemental phosphorus, equivalent to 0.08 pound per ton of product.(5)

At Plant 181, a different approach is taken towards phossy water wastes. Very large lagoons not only reduce the concentration of suspended solids in the phossy water, but also serve to slowly oxidize much of the elemental phosphorus to phosphates. Subsequent lime treatment of the lagoon overflow (after combining with other wastewater streams) precipitates not only the phosphates but also the fluorides in the water, thereby reducing the quantity of dissolved salts so that the water may be reused without a bleed. At this plant, the waste streams may be combined since all wastes are recycled without discharge.

A slightly different approach is taken at Plant 028. The phossy water is combined in a closed treatment and recycle system with calciner scrubber liquor. After settling of suspended solids and partial oxidation of phosphorus in a pond, lime treatment is used to precipitate dissolved phosphates and fluorides. Upon subsequent settling, the clarified (but still phossy) water is reused as calciner scrubbing water. Fresh makeup water is used for the phosphorus condenser. The key to this scheme, which results in zero discharge of phossy water, is that the quantity of water vaporized in the calciner scrubber (in cooling the calciner tail gases) exceeds the quantity of phossy water in the raw waste load, so that fresh water may be continuously added to the loop without discharging any contaminated water.

Plant 159 achieves zero discharge of phossy water in a rather unique system. The completely segregated raw waste phossy water is sent to a clarifier in a manner similar to the TVA technique described above. The clarifier underflow of phosphorus sludge is treated in conventional ways, with complete return of the material to the process. The overflow from the clarifier is not recycled (as is the TVA practice, which requires a bleed discharge); but is sent to an evaporation pond.

In the approaches used by Plants 028 and 159, some or all of the phossy water is evaporated. This presents no hazard of toxic elemental phosphorus, since it is very rapidly oxidized to phosphate as soon as the protective water is removed.

In summary, this study came up with three different ways that existing plants are achieving zero discharge of phossy water.

3.4 Removal of Anions (Except Chlorides) From Acidic Wastes

Section 3.1 pointed out that neutralization of acid wastewaters with lime also precipitates the calcium salts of all acid wastes in this industry (with the exception of hydrochloric acid from PCl_3 and $POCl_3$ manufacture). This treatment, as was pointed out, is widespread throughout the non-fertilizer phosphorus chemicals industry, and represents a class of treatment technology

which has widespread validation and demonstration on plant-scale installations.

Other technologies for removing dissolved solids (except chlorides) are also presented in this section, with a somewhat lesser degree of full-scale validation than lime treatment.

3.4.1 Treatment of Phosphoric Acid Wastes

The standard treatment of these wastes is by neutralization and/or precipitation with lime (see Section 3.1). Hydroxylapatite, the final product of neutralization in an excess of lime and in a considerable excess of water, is formed:

$$6\ H_3PO_4 + 10\ Ca(OH)_2 \rightarrow 9\ CaO{\cdot}3\ P_2O_5{\cdot}Ca(OH)_2 + 18\ H_2O$$

Although this material is very insoluble, the reaction does not proceed to completion in practice unless a Ca/P mole ratio of at least 1.9 is reached. Moreover, the reactivity of the lime in precipitating the dissolved phosphate is strongly dependent upon the lime source and the slaking conditions. It has been found that freshly-slaked pebble quicklime can precipitate in excess of 97 per cent of the phosphate, whereas commercial hydrated lime (calcium hydroxide) or freshly-slaked ground quicklime only succeeded in a 73 to 80 per cent precipitation efficiency under the same conditions.(30)

A large body of literature has been developed in the lime treatment of domestic wastewaters for phosphate removal. The study performed by Black & Veatch for EPA(31) summarizes the efforts that have been sufficiently demonstrated to be applied to current municipal wastewater treatment projects. It is pointed out that the average concentration in domestic raw wastewater is about 10 ppm (expressed as elemental phosphorus). The domestic sources are about 1.6 g (3.5 lbs) per capita per year, one-third of which are from human excretions and two-thirds from synthetic detergents.

The existing practice achieves better than 90 per cent removal of the phosphates from domestic wastewater, reducing the concentration (expressed as PO_4) from 30 ppm to as low as 0.3 ppm.(31) At first glance, this seems to conflict with the fact that tricalcium phosphate (or hydroxylapatite) has a solubility of 25 ppm (equivalent to 15 ppm as PO_4). However, in a large excess of lime, the pH is sufficiently high (10 to 11) to reduce the solubility of this salt of a strong base and weak acid. The equilibrium

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3\ Ca^{2+} + 2\ PO_4^{3-} \overset{2H_2O}{\rightleftharpoons} 3\ Ca^{2+} + 2\ OH^- + 2\ HPO_4^{2-}$$

is driven to the far left (reducing phosphate solubility) by the addition of excess lime. The solubility of tricalcium phosphate may be theoretically

calculated as a function of pH (or of Ca:P ratio) using the ionization constants for H_3PO_4, $H_2PO_4^-$, and $HPO_4^=$ in conjunction with a solubility product for tricalcium phosphate (which may be calculated from solubility data in pure water).

This phenomenon, substantiated by full-scale operating data as reported by Black & Veatch[31], is summarized below:

pH	Phosphate Concentration of Filtered Effluent, ppm
9.0	5.7
9.5	1.4
10.0	0.6
10.5	0.3
11.0	0.2

The literature is replete with details of technology to achieve high removal efficiencies.[31-42] For example, thickened sludge recirculation to the neutralization tank has been found to seed the precipitation of calcium phosphate, resulting not only in better removal of dissolved phosphates but also in the growth of larger crystals for easier dewatering.[33]

Although lime treatment of phosphates has been the predominant route, ferric chloride and alum have also been extensively used. Ferric salts are most effective in the 4-to-5 pH range and aluminum salts are most effective in the 5-to-6 pH range, as opposed to the 10-to-11 range for lime. The mole ratio of Fe/P or Al/O should be around 2.0, the same as the Ca/P ratio with lime treatment.[31,32]

The use of lanthanum salts has recently been demonstrated to more effectively precipitate phosphates over a much wider pH range than calcium, ferric, or aluminum. The drawback is cost; the treatment system must recover and reuse the lanthanum.[35]

Another process for phosphate removal is adsorption by activated alumina with subsequent stripping with caustic and then regeneration of phosphate-free caustic by lime precipitation.[34,36] Ion exchange has also been investigated.[34]

One interesting process for phosphate removal is borrowed from a commercial process for HCl-acidulation of phosphate rock.[4] Phosphoric acid is recovered by solvent extraction, using C_4 and C_5 primary alcohols such as n-butanol and isoamyl alcohol. The chloride-free phosphoric acid is then extracted from the organic phase by water washing, the solvent is recycled, and the pure phosphoric acid may be concentrated by evaporation of water. This treatment

method appears attractive for application to the food-grade calcium phosphate suspended waste streams. The suspended solids may be dissolved by HCl addition, and solvent extraction may be used to regenerate phosphoric acid for return to the process.

3.4.2 Treatment of Acidic Fluoride Wastes

Acidic fluoride wastes are generated by the phosphorus production segment of the industry and by the defluorination of wet-process acid in the manufacture of animal-feed grade calcium phosphates. These wasted waters containing large quantities of hydrofluoric, fluosilicic and silicic acids are neutralized with lime (which breaks down H_2SiF_6 at high pH) to precipitate calcium fluoride and gelatinous hydrated silica. Lime treatment is standard operating technology at Plants 028, 159, 181 and 182.

Like lime treatment of phosphoric acid, lime treatment of acidic fluoride wastes is enhanced by the decreased solubility of CaF_2 at high pH:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+} + 2F^- \overset{2H_2O}{\rightleftharpoons} Ca^{2+} + 2OH^- + 2HF$$

The equilibrium is driven to the far left by the addition of excess lime. The theoretical solubility of CaF_2 may be calculated in much the same manner as outlined for $Ca_3(PO_4)_2$, using the ionization constant of HF and the pure-water solubility data for CaF_2.

There has been recent commercial interest in recovering the fluoride values in acidic wastewaters. Two commercial processes have been developed to manufacture hydrofluoric acid[43], and one to manufacture synthetic cryolite for the aluminum industry.[7]

3.4.3 Treatment of Acidic Sulfite, Sulfate, and Phosphate Wastes

These acids are components of the waste streams from the phosphorus-consuming segment of the industry; and sulfuric acid is also a constituent of the wastes from the phosphorus-production segment. The sulfurous and phosphorous acids may be partially oxidized prior to treatment to sulfuric and phosphoric acids.

The neutralization and precipitation of the slightly soluble calcium salts is exactly comparable to the treatment of acidic phosphate and fluoride wastes. The solubilities of calcium sulfite and of calcium phosphite are repressed by excess lime as in the previously-discussed cases, but the solubility of calcium sulfate (a salt of a strong base and a strong acid) is not affected by pH.

3.5 Removal of Suspended Solids

The raw waste streams from the phosphorus-producing segment and from the phosphate segment of the industry contain considerable quantities of suspended solids. Moreover, the chemical treatment of acidic wastes described in the previous section produced, in many instances, additional suspended solids.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids. They are in use at plants 006, 028, 119, 159, 181 and 182.

The size and number of settling ponds differ widely depending on the settling functions required. Waste streams with small suspended solids loads and fast settling characteristics can be cleared up in one or two small ponds; others with heavier suspended solids loads and/or slower settling rate may require 5 to 10 large ponds. Most settling ponds are unlined, but the technology exists for lined ponds.

Although not as widely used as settling ponds, tanks and vessels are also employed for removal of suspended solids in the phosphorus chemicals industry. They are in use at TVA (Muscle Shoals, Alabama)[5] and at plants 003, 006, 028 and 159.

Commercially these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. They also have internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide more efficient performance. This feature plus the positive containment and control and reduced rainfall influence (smaller area compared to ponds) should lead to increasing use of vessels and tanks in the future, especially where a plant is short of available land for settling ponds.

Filtration equipment, such as plate-and-frame pressure filters, pressure or vacuum leaf filters, rotary vacuum filters, and pressure tubular filters, has been widely used in the chemical and waste treatment fields for many years. The batch-type filters find most use in polishing applications, to completely remove small quantities of suspended solids, since the labor-intensive blowdown operation is dependent upon cake volume. These filtrations are common for collection of toxic solid wastes, such as arsenic sulfide from food-grade phosphoric acid. Continuous rotary vacuum filters find general applicability in dewatering sludges with high concentrations of solids. Sand-bed filtration also finds increasingly-widespread use.

Filtration is in use at plants 006, 075 and 119 in this industry. In general, filtration is not economically attractive for huge quantities of wastewater (except for sand-bed filtration). It is usually preceded by a gravity thickening operation so that it treats the thickened sludge which is only a

small volumetric percentage of the total wastewater flow.

Centrifugation, in use at Plant 003 and at the TVA installation[5], is an alternate means for mechanical dewatering of relatively low-flowrate sludges, and has made major recent inroads into the domestic wastewater treatment field. The continuous solid-bowl centrifuge, as its name implies, provides for continuous removal of the cake, and its design reaches a compromise between solids recovery and cake dryness. The basket solid-bowl centrifuge, on the other hand, discharges cake intermittently, and the dewatering and cake-drying portions of the cycle may be separately controlled. Perforated-bowl centrifuges are really centrifugal filters. The solid-bowl machines offer the significant advantage over filters that blinding of a medium is removed as a problem area.

3.5.1 Dewatering of Lime-Precipitated Phosphates

Although (as previously discussed) lime can be used to effectively precipitate phosphates from solution to reduce the concentration to 0.3 ppm or less (as PO_4), the lime-precipitated phosphates do not dewater readily, but form a water-trapping gel structure. After 24 hours of settling, clarified effluents still may have 15 to 50 ppm of suspended solids. This can be significantly improved by increasing the detention time to 7 days, but the suspended solids content may still be 5 ppm or greater. In the phosphorus chemicals industry, settling ponds with 7 days or longer detention times (equivalent to an overflow rate of 420 lpd/m^2 (10 gpd/ft^2) at a nominal depth of 3 m (10 ft) are used.[30] It has also been reported that the settling characteristics are strongly dependent upon the initial concentration of phosphate ion. An initial concentration of 75,000 ppm resulted in a compacted settled slurry density 3 to 5 times higher than if the initial concentration was 1,500 ppm.[30]

Where sufficient land area for large settling ponds is not available, average removal efficiencies of 80 to 95 per cent have been obtained with mechanically-raked gravity thickeners.[31-33] A typical thickener design has a 2-hour detention time and an overflow rate of 42,000 lpd/m^2 (1,000 gpd/ft^2).[31,33]

Synthetic organic, water-soluble, high molecular weight polyelectrolytes have achieved great success in flocculation and clarification and in sludge conditioning prior to centrifugation or filtration.[32] A polymer dosage of 0.05 kg per kkg of dry sludge solids (0.1 lb/ton), or about 1 ppm of a 2 per cent slurry, may achieve 85 per cent removal of suspended solids at a detention time of 2 hours, with a 12 per cent solids content in the thickened sludge.[31-33] If this thickened sludge were then vacuum-filtered, a cake of 30 per cent solids could be obtained with a solids content in the filtrate of 0.5 ppm or less.[30]

The following may be a typical performance chart for an influent sludge containing 100 liters of water:

	Influent	Thickener Overflow	Thickener Underflow	Filter Cake	Filtrate
Water, Liters	100	84	16	5.1	10.9
Suspended Solids, Kg	2.56	0.38	2.18	2.18	5×10^{-6}
Suspended Solids Concentration	2.5%	0.45%	12%	30%	0.5ppm

The dewatered cake, containing 85 per cent of the original solids, may be landfilled. The filtrate, when combined with the thickener overflow, would consist of 95 per cent of the original water quantity and would have a suspended solids concentration of 4,000 ppm.

A much clearer effluent could be obtained, of course, if all of the influent wastewater were directly filtered. Such is the practice at Plant 006, which achieves an average phosphate removal efficiency of 95 per cent.

Mechanical dewatering of lime-precipitated phosphates by centrifugation was attempted, but it proved unsuccessful because the highly thixotropic cake plugged the solids-removal screw.(30)

Because an excess of lime is used in the precipitation of the phosphates, the effluent from the ponds or from mechanical thickening and dewatering would have a high pH, typically 10 to 11. This effluent could be partially carbonated (with CO_2) to reduce the pH to 8.0 to 8.5 prior to discharge,(31,33) with another filtration step to remove the calcium carbonate precipitate. Alternately, it has been shown that subsequent activated sludge treatment of high-pH wastewater at municipal treatment plants lowers the pH due to biologically-released CO_2 from the oxidation of organic material.(31)

3.6 Removal of Chlorides

3.6.1 Ion Exchange and Demineralizations

Ion exchange and demineralizations are usually restricted in both practice and costs to total dissolved solids levels of 1000 to 4000 ppm or less.

An ion exchanger may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge and an exchangeable ion carrying an opposite charge. The inert matrix is usually cross-linked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

$$RSO_3H + NaCl = RSO_3Na + HCl$$

$$RCO_2H + NaCl = RCO_2Na + HCl$$

The above reactions are reversible and can be regenerated with acid.

Anion exchangers use basic group such as the amino family.

$$RNA_3OH + NaCl + RNA_3Cl + NaOH$$

This is also a reversible reaction and can be regenerated with alkalies. The combination of water treatment with both cation and anion exchangers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 9 gives the level of total dissolved solids that is achieved.

Special ion exchange systems have been developed for treating high dissolved solids content (more than 1000 mg/liter total dissolved solids), minimizing regenerant chemicals costs.

3.6.2 Reverse Osmosis

The phenomenon of osmosis has its explanation in thermodynamic equilibrium and free energy concepts. Essentially, when a semi-permeable membrane separates a pure liquid and solution of dissolved material in the same liquid there is a net migration of the pure liquid to the solution, driven by the free energy difference between the two sides of the membrane. Equilibrium is reached only when the liquids on each side of the membrane are of the same composition or sufficient additional pressure is applied on the solution side of the membrane to counterbalance the osmotic driving force. Application of additional pressure on the solution side reverses the direction of osmotic flow through the membrane and results in concentration of the solution and migration of additional pure liquid to the pure liquid side. This is reverse osmosis. It may be looked at as pressure filtration through a molecular pore-sized filter.

The small pore size of the reverse osmosis membrane is both its strength and its weakness. Its strength comes from the molecular separations that it can achieve. Its weakness comes from the criticalness it has to blinding, plugging, and chemical attack. Acidity, suspended solids, precipitations, coatings, dirt, organics and other substances can make it inoperative. Membrane life is critical and unknown in many mediums.

With these restrictions there is little wonder that its industrial applications

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TABLE 9 Water Quality Produced by Various Ion Exchange Systems

Exchanger Setup	Residual Silica ppm	Residual Electro-lytes, ppm	Specific Resistance ohm-cm @ 25 C
Strong acid cation + weak-base anion	No silica removal	<3	<500,000
Strong-acid cation + weak-base anion + strong-base anion	<0.01-0.1	<3	<100,000
Strong-acid cation + weak-base anion + strong-acid cation + strong-base anion	<0.01-0.1	0.15-1.5	<1,000,000
Mixed bed (strong-acid cation + strong-base anion)	<0.01-0.1	<0.5	1-2,000,000
Mixed bed + first or second setup above	<0.05	<0.1	3-12,000,000
Similar setup as immediately above + continuous re-circulation	<0.01	<0.5	18,000,000

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are few. Fortunately, the phosphorus chemicals industry water purification needs are similar to those of the areas where reverse osmosis has been shown to be applicable -- treatment of brackish water and low (500 ppm to 20,000 ppm) dissolved solids removal. Organics are usually absent, suspended solids are low and can be made low rather easily, acidity is easily adjusted, and the dissolved solids are similar to those in brackish water -- sodium chlorides, sulfates and their calcium counterparts.

3.6.3 Evaporation Ponds

Plant 159 utilizes an evaporation pond for disposal of phossy water from phosphorus manufacturing. They may also be reasonably used for other wastewater disposal where the wastewater quantities are not overwhelming.

The size of an evaporation pond depends upon the climatic differential between evaporation and rainfall:

Evaporation-Rainfall Differential	Pond Area
0.6 m/yr (2 ft/yr)	0.060 ha/cu m/day (560 acres/MGD)
1.2 m/yr (4 ft/yr)	0.030 ha/cu m/day (280 acres/MGD)
1.8 m/yr (6 ft/yr)	0.020 ha/cu m/day (190 acres/MGD)

Evaporation ponds may be either unlined or lined, and should be diked. Use is often made of natural pits, valleys or ponds.

Conventional evaporation ponds are not, or course, among the useful treatments in areas where the rainfall exceeds the evaporation. However, surface aerators (commonly used for aerated lagoons in secondary treatment of organic wastes) can significantly increase the evaporation from a pond by increasing the water/air surface area.

3.6.4 Single-Effect and Multiple-Effect Evaporators

For the treatment of small waste streams, single-effect evaporators are characterized by low equipment costs and by inherent reliability, at the expense of high steam requirements. Conventional multiple-effect evaporators, with 2 to 6 effects, have somewhat higher capital costs, but require much less steam.

Evaporation is a technology, of course, that is aptly demonstrated throughout the chemicals process industry (although not extensively for the sole purpose of waste treatment), and as such meets the requirements of being currently available.

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SECTION VIII

COST, ENERGY AND NON-WATER QUALITY ASPECTS

1.0 INTRODUCTION

The control and treatment technologies applicable to the raw wastes of the non-fertilizer phosphorus chemicals industry were discussed in Section VII of this report. In this Section, each of these technologies is reviewed from the following standpoints:

* The cost of applying the technology.
* The energy demands of the technology.
* The impact of the technology upon air quality, solid waste management, noise and radiation.
* The recovery and subsequent use of process materials from raw waste streams, as a result of applying the technology.

In Supplement A of this report (not included in this volume), a representative hypothetical plant for each chemical produced in the industry is synthesized. Cost-effectiveness data for the plant are developed; the cost in terms of both investment cost and equivalent annual cost, and the effectiveness in terms of the reduction in aqueous waste quantities. The discussion of costs and benefits in this Section, however, is formulated to be more generally useful in evaluating the economics for any particular plant within the industry. Costs for a specific plant may be significantly influenced by the following factors which cannot all be incorporated into a single hypothetical plant:

1. The degree of freedom, which personnel of each plant must retain, to choose among the alternative control and treatment technologies presented in Section VII, to choose from technologies not presented in this report, and to choose any combination or permutation of these technologies.

2. The cost tradeoffs, which are unique for each plant, between in-process controls and end-of-process treatments; with material recovery being an important parameter.

3. The real raw waste load for each plant, which may be appreciably different (in either direction) from the standard raw waste loads as presented in Section V. In particular, much greater plant-to-plant variability was observed with respect to production-normalized raw wastewater quantities than with respect to production-normalized raw quantities of polluting constituents.

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4. The degree of pollution abatement already installed and practiced at a particular plant. The thrust of this program was to identify exemplary plants within each segment of the industry, rather than to survey the entire industry to analyze how much must still be accomplished by non-exemplary plants.

5. The physical characteristics of each particular plant, which vary widely in the industry and which significantly affect the cost of applying control and treatment technologies. Among these physical characteristics are:

   * Plant age, size, and degree of automation.
   * Plant layout (i.e., can in-process controls be physically installed between existing units).
   * Plant distances and topography (i.e., what are the installation and operating costs of recycle technologies).
   * Climatic factors (temperature and evaporation/rainfall).
   * Esthetic factors (i.e., is a settling pond locally acceptable?).
   * Land Availability (primarily a factor in applying settling pond and evaporation pond technologies).

6. The degree to which a plant is integrated with other production departments would significantly affect the cost of applying control and treatment technologies. Can waste materials from one department be used in an adjoining department (i.e., mutual neutralization of acid and alkaline wastes)? Can common treatment facilities be built (trade-off between economies of scale vs. reversing the principle of segregation of wastes)? Are the wastewater sewers from adjoining departments readily separable?

7. The feasibility and attractiveness of joint municipal/industrial wastewater treatment, which is a highly local evaluation to be made. Increasingly more examples of such dual treatment are being reported. (59,60,62).

8. The local solid waste management situation. The sludges from applying wastewater treatment technologies may be landfilled at highly different costs, depending upon the local availability of disposal sites and the distances involved.(63,64)

In appreciation of all of the above factors, the discussion of costs in this Section is formulated to be generally useful in evaluating the economics for any particular plant within the industry.

1.1 Current Selling Prices

Table 10 lists the current selling prices of the chemicals within this industry. These data are useful as a yardstick for measuring the economic impact of achieving pollution control.

1.2 Capital Cost Basis

The capital costs quoted in this Section have been adjusted to 1971 dollars, using the Chemical Engineering Plant Cost Index (1957-59 = 100; 1971 = 132.2). Only equipment specific to waste treatment is discussed in detail; There are sufficient sources already available for estimating standard items such as pipe, pipe fittings, tanks, pumps, mixers, etc.

2.0 IN-PROCESS CONTROLS

The cost of these controls are perhaps the most difficult to generalize, since they are almost wholly dependent upon the existing equipment configuration in any particular plant.

2.1 Segregation of Waste Streams

First, a plant must be surveyed to pinpoint the sources of both process water and non-contact cooling water. At one plant, there were a great many points where process water entered a common sewer, but there were relatively few cooling water sources.(30) It was much more economical to divert the cooling water to a new and separate collection system than to adopt the reverse strategy. The project costs for such a retrofit would be highly labor-intensive, especially since the construction must proceed without unduly disrupting production schedules. Other than capital recovery and associated annual costs, the annual costs would consist of a small maintenance cost and no costs for operating labor, materials or power.

There would be no effect of this project on energy demands, since plant sewers are normally gravity-flow. There would be no adverse non-water quality impacts of this project.

2.2 Recycle of Scrubber Water

The capital costs would be to provide a surge tank, a recycle pump, and associated piping. The surge tank need not be large; a 15-minute residence time should suffice. The power costs and energy use for the pump should not greatly exceed the corresponding values presently utilized to provide fresh scrubber

TABLE 10. Current Selling Prices of Phosphorus Chemicals

Source: Chemical Marketing Reporter, June 25, 1973

CHEMICAL	GRADE	SELLING PRICE	
		$/Metric Ton	$/Short Ton
White Phosphorus		419	380
Phosphoric Acid (Furnace)	75% Commercial & Feed	164	149
	80% Commercial & Feed	176	160
	85% National Formulary	194	176
Phosphorus Pentoxide		441	400
Phosphorus Pentasulfide		299	271
Phosphorus Trichloride		292	265
Phosphorus Oxychloride		270	245
Sodium Tripolyphosphate	Technical	179	162
	Food	270	245
Monocalcium Phosphate	Anhydrous Food	314	285
Dicalcium Phosphate	U.S.P Food	286	259
	Feed	82	74
Tricalcium Phosphate	NF Precip.	315	286

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water at comparable flow rates; in any event they are small since scrubber flow rates are small.

2.3 Dry Dust Collection

Based upon data furnished by the personnel of Plant 007, the capital cost of high-temperature baghouses for this 91 kkg/day (100 tons/day) plant was $350,000. The annual operating and maintenance costs, other than capital recovery, taxes and insurance, is estimated at 6 per cent of the capital cost. A credit to the annual cost is the value of recovered material; the quantity might be estimated as 2 to 5 per cent of the production rate, since baghouses recover virtually all dusts. The power requirements for the fans and shakers are small, and are usually comparable to the pump power requirements for the liquid scrubbing systems they replace. Since the recovered dusts are almost always utilized in the process, there is no adverse impact upon solid waste management.

2.4 Refrigerated Condensers

The condensers are standard items, and in practice the existing condensers may be used. The refrigeration supply is standard equipment, and rather expensive in terms of capital costs. An added cost would be the insulation of existing coolant lines and of the condenser. The power requirement for the refrigeration compressor could be moderately high. There would be no impact upon non-water quality aspects.

2.5 Inert-Atmosphere Casting for P_2S_5

This is a relatively expensive control technique, requiring major revisions not only of the casting equipment but also of the basic casting procedures. There would be some small power requirement either for inert-gas blowers or for vacuum pumps. The annual cost of the inert gas (assuming it is not recycled) must be estimated.

2.6 Housekeeping and Containment

Like the previously-discussed project of water segregation, housekeeping and containment capital costs are labor-intensive and depend to a very large extent upon the existing plant configuration. A point of reference might be taken from the experience of one 360 kkg/day (400 tons/day) plant which expended $160,000 for isolation and containment (trenches, sewers, pipelines, sumps, catch basins, tanks, pumps, dikes and curbs). The need to attend to many small sources of leaks and spills reduces the economies of scale. The power requirements are minimal, limited to small sump pumps. No adverse non-water quality impacts arise from this control technique.

3.0 TREATMENT OF SPECIFIC WASTE CONSTITUENTS

3.1 Neutralization of Acidic Wastewaters and Precipitation of Calcium Salts

A general cost factor for neutralization is 1.3 to 5.3 cents per cu m (5 to 20

cents/1,000 gallons)[32,65]. However, the cost for lime is directly dependent not upon the wastewater quantity but upon the total acidity. The data of Table 3, with a lime cost of $22/kkg ($20/ton), can be used to calculate this cost.

Neutralization tanks are usually small, with residence time varying from 30 seconds[31] to 30 minutes.[30] The installed cost of these tanks may be approximated by:

$$\text{Capital Cost} = \$15{,}000 \left(\frac{\text{GPD}}{10{,}000}\right)^{0.2}$$

(Note: ℓ/day = 3.785 x GPD)

The power requirements for mixing are rather nominal. Assuming subsequent sedimentation or other dewatering operations, the neutralization step alone does not have any adverse non-water quality impacts.

3.2 Treatment of Arsenic-Rich Residues

The cost of this solvent is rather nominal because the quantities of waste involved are only a very small fraction of the production volume, and because the solvent (trichloroethylene) is reused; despite the high unit costs which is more than 10 cents/cu m (40 cents/1,000 gal).[65] There is virtually no power requirement. There is, however, a very substantial impact upon solid waste management, since the residues are extremely toxic and must be disposed of in special ways. The quantity involved is 0.05 Kg of $AsCl_3$ per kkg of product PCl_3 (0.1 lbs/ton).

3.3 Control and Treatment of Phossy Water

Control and treatment of phossy water is a universal practice at phosphorus-producing plants. Although several different methods were observed, every plant prevents the discharge of virtually all elemental phosphorus. This technology is therefore so universally applied that costs need not be estimated -- the price has already been paid. Similarly, a discussion of energy and of non-water quality aspects would be academic.

3.4 Removal of Suspended Solids

3.4.1 Settling Ponds

Using a detention time of 7 days and a depth of 3 m (10 ft), the calculated overflow rate is 0.42 cu m/day/m^2 (10 gpd/ft^2). This is equivalent to 4,200 cu m/day/hectare (435,600 gpd/acre).

The capital costs for small unlined ponds, with areas from 0.4 to 2 hectares

(1 to 5 acres) can be estimated as[67-69]:

$$\text{Capital Cost} = \$50{,}000 \times \text{Acres} - \$8{,}000 \times (\text{Acres})^2$$

(Note: Hectares = 0.405 x Acres)

Because diking is a large portion of pond costs, and because the dike length increases much more slowly than pond area, larger ponds are considerably cheaper per unit area. For large unlined ponds of 40 to 1,000 hectares (100 to 2,400 acres), the capital cost is $2,500 to $12,500 per hectare ($1,000 to $5,000 per acre).[66]

For lined ponds, the additional installed capital cost for a 30-mil PVC liner is $21,500 per hectare ($8,700 per acre).[68,69]

By using the above overflow rate and the above pond costs per unit area, a pond cost based on wastewater flow rate may be calculated.

Settling ponds utilize no energy. The solids do, however, collect on the bottom and must either be periodically removed (creating a solid waste disposal problem); or the filled pond may be abandoned and replaced with a new one (creating a land use problem).

3.4.2 Mechanically-Raked Clarifiers and Thickeners

A general cost for gravity thickening is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons.[65]

The installed cost of mechanically-raked clarifiers and thickeners with capacities of 38 cu m/day (0.01 to 10 MGD) can be estimated as[70,71]:

$$\text{Capital Cost} = \$95{,}000\ (\text{MGD})^{0.4}$$

(Note: Cu m/day = 3,785 x MGD).

Where polymeric flocculents are used, the additional cost amounts to $4 per kg of flocculent ($1.80/lb).[32] The dosage rate is nominally 0.05 kg/kkg of dry sludge solids (0.1 lbs/ton).

The power requirements are nominal, since the rake has a very long period of revolution. Additional nominal power requirements arise from sludge pumping and clarifier overflow pumping.

This treatment has (by definition) a solid waste impact, since its function is the removal of suspended solids. The sludge from thickeners may be 85 to 92 per cent moisture. If the quantities are small, this sludge may be directly transported to landfills. Alternately, it may be dewatered on sand drying beds or

mechanically (filters or centrifuges) to 60-70 per cent moisture before landfilling. The quantity to be landfilled is therefore a very strong function of the degree of dewatering after thickening.

3.4.3 Vacuum Filtration and Centrifugation

The costs of these two mechanical dewatering techniques are competitive. A general cost for either is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).(65)

The installed capital costs for either vacuum filters or centrifuges are as follows(70,71).

Capacity, MGD	cu m/Day	Installed Cost
0.01	38	$25,000
0.1	378	25,000
1	3785	200,000
10	37850	750,000

Polymeric flocculents are often used to condition the sludge prior to dewatering. Their costs were discussed in the previous paragraph.

The power requirements for vacuum filtration are moderate; they include the sludge pump, the flocculent pump, the rotating conditioning tank, the vacuum filter drum drive, the sludge agitator below the filter drum, the vacuum pump, the filtrate pump and the cake conveyor belt. Centrifuges have much larger power requirements, since the sludge must be accelerated to hundreds or several thousands of G's. At high speeds, the windage losses (air friction) of centrifuges are considerable. Large centrifuges may require 40 to 75 Kw (50 to 100 HP) of power. Auxiliary power is also required for sludge pumping, flocculent pumping, centrate pumping, the cake scraper, and the cake conveyor belt.

Vacuum filters and centrifuges have a beneficial impact upon solid waste management. Rather than landfilling 12 per cent sludge, these devices drastically reduce the solid waste quantity by producing a 30 to 40 per cent cake.

Centrifuges have a moderately adverse impact with regard to noise pollution, since they run with a characteristic high-speed whine that is annoying to the human ear. Vacuum filtration is also a noise contributor since vacuum pumps are noisy machines.

3.4.4 Landfilling of Solid Wastes

The disposal costs for solid wastes are highly dependent upon the hauling distance.

The landfill operations alone may cost $6 or more per kkg (or per ton) for small operations and $2 to 4 per kkg (or per ton) for larger operations.

Several pertinent papers have recently been published on the subject of solid waste management in the chemical industry.(63,64)

Solid waste hauling and the material handling operations at landfills are energy-consuming operations.

3.5 Removal of Chlorides

3.5.1 Demineralization and Reverse Osmosis

These treatments are costly, over 10 cents per cubic meter (40 cents per 1,000 gallons).(65)

The installed capital costs can be calculated from:

a. Demineralization, Cap. Cost = $280,000 $(MGD)^{0.75}$

b. Reverse Osmosis, Cap. Cost = $480,000 $(MGD)^{0.75}$

Hence, the capital costs for reverse osmosis are nearly double those for demineralization.

The operating costs (not including capital recovery costs) are:

a.	Demineralization,	20 cents/1,000 gal @ 1,000 ppm TDS
		40 cents/1,000 gal @ 2,000 ppm TDS
b.	Reverse Osmosis,	38 cents/1,000 gal @ 0.01 MGD
		20 cents/1,000 gal @ 0.1 MGD
		14 cents/1,000 gal @ 1 MGD

Neither demineralization nor reverse osmosis require a great deal of power, and neither has significant non-water quality impact.

3.5.2 Solar Evaporation Ponds

The installed costs of solar evaporation ponds (on the basis of pond area) are essentially the same as the costs for settling ponds presented in paragraph 3.4.1. The pond area depends in this case upon the climatic differential between evaporation and rainfall:

Evaporation-Rainfall Differential	Pond Area
0.6 m/yr (2 ft/yr)	0.060 ha/cu m/day (560 acres/MGD)
1.2 m/yr (4 ft/yr)	0.030 ha/cu m/day (280 acres/MGD)
1.8 m/yr (6 ft/yr)	0.020 ha/cu m/day (190 acres/MGD)

The power requirements and non-water quality aspects of solar evaporation ponds are the same as for settling ponds. However. since the residue in this case is soluble, extra disposal precautions must be taken to prevent leaching into groundwaters.

3.5.3 Single-Effect and Multiple-Effect Evaporators

The installed capital and operating costs for single-effect evaporators and for a 6-effect evaporator (all stainless-steel construction) are as follows:

Capacity, GPD	Installed Capital Costs		O & M Costs, $/1,000 gal	
	1 Effect	6 Effects	1 Effect	6 Effects
10,000	8,000		5.64	
50,000	28,000		5.51	
100,000	45,000	177,000	5.45	1.30
250,000	80,000	373,000	5.39	1.22
500,000	146,000	665,000	5.36	1.18
1,000,000	267,000	1,225,000	5.33	1.14

(Note: Liters = 3.785 x Gallons)

The energy requirements for single-effect evaporators are 555 kg-cal per kilogram of water evaporated (1,000 Btu/lb); while the 6-effect evaporator requires 100 kg-cal per kilogram of water evaporated (180 Btu/lb). The non-water quality aspects are the same as for solar evaporation ponds.

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE, LEVEL I EFFLUENT GUIDELINES AND LIMITATIONS

1.0 INTRODUCTION

The effluent limitations which must be achieved by July 1, 1977 are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the non-fertilizer phosphorus chemicals industry, this level of technology is based on the best existing performance by exemplary plants of various sizes, ages and chemical processes within each of the industry's categories. In some cases where no truly exemplary plants were surveyed, this level of technology is based upon state-of-the-art unit operations commonly employed in the chemical industry.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself. Examples of in-process control techniques which are used within the industry are:

- manufacturing process controls
- recycle and alternative uses of water
- recovery and/or reuse of wastewater constituents
- dry collection of airborne solids instead of (or prior to) wet scrubbing.

Consideration was also given to:

a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application;

b. The size and age of equipment and facilities involved;

c. The process employed;

d. The engineering aspects of the application of various types of control techniques;

e. Process changes;

f. Non-water quality environmental impact (including energy requirements).

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2.0 GUIDELINES FOR NON-CONTACT COOLING WATERS AND BLOWDOWNS

A fundamental distinction exists between process water (defined as water which comes into contact with raw materials, intermediates, products, by-products, or gaseous, airborne, or solid wastes); and non-contact cooling water and blowdowns. In the industry today, segregated cooling water is separately discharged in many cases; in other situations, cooling and process waters are mixed prior to treatment and discharge.

The recommended Level I limitations on the discharge of non-contact cooling water and blowdowns are as follows:

(a) An allowed discharge of all non-contact cooling waters provided that the following conditions are met:

(1) No toxic or hazardous pollutants are added. Cooling waters discharged must not have levels of chromate or other toxic pollutants higher than that of the intake water or receiving water, whichever is lower.

(2) Thermal pollution be in accordance with local water quality standards.

(3) No process waters be added to the cooling waters prior to discharge.

(4) All non-contact cooling waters should be monitored to detect leaks from the process and provisions should be made for emergency treatment prior to release.

(b) An allowed discharge of water treatment, cooling tower and boiler blowdowns provided these do not contain toxic or otherwise hazardous materials such as chromium or cadmium, and are within the required pH range of 6 to 9 as measured both as a daily maximum and as a monthly average.

3.0 PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, byproducts, or gaseous, airborne, or solid wastes. All values of guidelines and limitations presented below for total dissolved solids (TDS), total suspended solids (TSS), heavy metals and toxic pollutants and other parameters are expressed as monthly averages in units of pounds of parameter per ton and kilograms of parameter per metric ton of product produced except where expressed as a concentration. Where a zero appears

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for a parameter applicable to a discharge of process wastewater, the zero signifies no increase in the parameter above the level of the intake water or receiving water, whichever is lower. Zero discharge of process wastewater means that no process water be discharged from the plant into surrounding waterways.

Based upon the information contained in Sections III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best practicable control technology currently available in the non-fertilizer phosphorus chemicals industry.

3.1 The Phosphorus Production Segment

3.1.1 Phossy Water

Because of the extremely toxic nature of elemental phosphorus, it is standard practice within the industry to maintain tight control over the discharge of phossy water, as discussed in Section VII-3.3.

TVA at Muscle Shoals, Alabama[5] segregates phossy water from all other process and cooling waters, treats the phossy water, and then recycles the treated water back to the process. The treatment consists of coagulation and sedimentation using a synthetic flocculent, with total use (without discharge) of the phosphorus-rich clarifier underflow. The clarifier overflow is recycled back to the process, but because of the buildup of dissolved solids, about 6 per cent of this clarified water is bled off. In addition to containing significant quantities of dissolved phosphates and fluorides, this blowdown waste contains some suspended solids and the following quantity of elemental phosphorus[5]:

Blowdown Quantity:	330 l/Kkg (80 gal/ton)
P_4 Concentration:	120 ppm
P_4 Discharged:	0.04 Kg/Kkg (0.08 lbs/ton)

This quantity is less than 0.5 per cent of the raw waste load of elemental phosphorus, 9 Kg/Kkg (18 lbs/ton).

It is apparent, however, that existing practicable technology can eliminate the requirements for any discharge at this TVA plant. Lime treatment of the blowdown followed by sedimentation of the precipitated phosphates and fluorides would remove the materials necessitating a blowdown, so that this treated blowdown could be recombined with the remainder of the clarified phossy water for return to the process.

There are three examples of plants which have achieved zero discharge of

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phossy water.

Plant 159 removes the bulk of the elemental phosphorus by coagulation and sedimentation, with total processing and use of the clarifier underflow in a manner similar to TVA. Instead of recycling the clarified phossy water, however, Plant 159 uses an evaporation pond, thereby preventing the discharge of any elemental phosphorus (or the contained dissolved solids and suspended solids).

Plant 028 achieves zero discharge of phossy water by combining the phossy water wastes with calciner scrubber wastes in a closed treatment and recycle system. The buildup of other impurities (which would prevent complete recycle) is avoided by lime treatment and sedimentation; and the combination of the two waste streams ensures that no excess (contaminated) water builds up since more water is evaporated in the calciner scrubber part of the loop than is generated in the phossy water part of the loop.

Plant 181 achieves zero discharge of phossy water in a manner akin to the Plant 028, that is by exploiting the net consumption of water in other parts of the plant to accommodate the net production of phossy water. By combining all waste streams and with appropriate lime treatment and sedimentation to remove enough dissolved and suspended solids to avoid the need for a blowdown, the entire water system of this plant (including the phossy water) is totally recycled.

Hence, three plants have recognized the extreme toxicity of elemental phosphorus in any discharge and have also recognized that no practicable treatment system can remove a sufficient amount of elemental phosphorus to permit effluent discharge of phossy water wastes. They have all solved this dilemma by evaporating sufficient phossy water rather than by discharge. One plant uses an evaporation pond, while two others exploit other process heat loads for in-process water evaporation.

In view of this clear-cut demonstration within the industry, it is recommended that the Level I Guidelines for phossy water wastes be zero discharge.

3.1.2 Process Waters Other than Phossy Water

The standard techniques for treating the wastewaters from calciner scrubbers and from slag quenching are lime treatment and settling ponds, which perform the following functions:

* Neutralization of acid wastewaters
* Sedimentation of much of the original suspended solids in the wastewaters (silica, iron oxide, and others)

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* Precipitation and sedimentation of much of the phosphates, fluorides and sulfates which were dissolved in the original wastewaters.
* Dissipation of the process heat to the atmosphere during the extended residence in the settling ponds.
* Reduction in the wastewater quantity as a result of net evaporation during the extended residence in the settling ponds.
* Where phossy water is combined with these other process waters, some oxidation of the elemental phosphorus to phosphates is accomplished.

At Plant 181, the lime-treated water from all sources is clarified in settling ponds, and the clarified water is held in reuse water supply ponds. There is total recycle of all water at this plant, with zero discharge. Because phosphates and fluorides are removed by lime treatment and sedimentation, there is no requirement to bleed off water for the control of dissolved solids.

Under conditions of very abnormally-high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final reuse water supply ponds, thereby minimizing the quantities of pollutants even occasionally discharged. The recirculating water system runs at a water deficit, due to evaporation in the process and to net evaporation in the pond system. Hence, fresh makeup water is supplied, and can be controlled to compensate for temporary swings in the pond evaporation/rainfall balance.

The TVA plant at Muscle Shoals, Alabama[5] granulates the slag by quenching with a high-velocity jet of water which is recirculated from a sump in the slag pit. In this TVA operation, the cooling water and the scrubber liquors are used for makeup in slag quenching. The granulated slag effectively neutralizes these waters and also acts to filter out the scrubbed solids, which become part of the slag pile to be sold. Nearly all of the soluble phosphate and 95 per cent of the fluoride is removed by the slag, and the fluoride concentration is reduced to 30 ppm. Hence, TVA utilizes slag treatment instead of lime treatment, made possible because the slag is finely-divided. Sufficient wastewater treatment is obtained by TVA to enable the plant to completely reuse this water without any discharge.

Two other phosphorus plants which utilize lime treatment and sedimentation for process water treatment are Plants 028 and 159. Tables *11* and *12* list (respectively) the effluent concentrations and quantities discharged from these plants, neither of which recycle treated wastewater. There are three significant differences between these two plants:

* Plant 028 discharges into the same waterway as the plant

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TABLE II - Effluent from Plant 028 (Discharge No. 001)

Effluent Flowrate = 103-200 l/kkg (24,700 gal/ton)

Notes: 1. This Discharge is from Cooling Water and Dust Collector Water.
2. There is Zero Discharge of Phossy Water and Calciner Scrubber Water

	Water & Wastewater Analysis				Net Effluent Qty Kg/Kkg		Net Effluent Qty Lbs/ton	
Constituent	Units	Intake	Effluent Plant Data	Effluent Ind. Data	Plant Data	Independent Data	Plant Data	Independent Data
pH	-	-	7.3-9.5	7.55	-	-	-	-
Turbidity	FTU	26	32	30	-	-	-	-
Conductivity	$\frac{\mu mhos}{cm}$	359	408	300	-	-	-	-
TSS	mg/l	15	15	20	-	0.5	0	1
TDS	mg/l	160	202	176	4	2	9	3
$CaCO_3$ Alkalinity	mg/l	116	110	130	(-1)	1	(-1)	3
$CaCO_3$ Acidity	mg/l	-	-	-	-	-	-	-
Chloride	mg/l	<0.1	4.1	8	0.4	0.8	0.9	1.6
Fluoride	mg/l	0.19	1.14	0.87	0.10	0.07	0.20	0.14
Sulfate	mg/l SO_4	6.4	13.8	26	0.8	2.1	1.5	4.1
COD	mg/l	2.0	53.5	25	5.3	2.4	10.6	4.8
Total Hardness	mg/l	116.7	129.7	160	1	4	3	8
Total Phosphate	mg/l PO_4	1.2	2.4	-	0.12	-	0.25	-
Ortho Phosphate	mg/l PO_4	1.2	2.4	2.9	0.12	0.18	0.25	0.35

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TABLE 12.- Effluent from Plant 159

Notes: 1. There is Zero Discharge of Phossy Water
2. These data are Plant Data, Not Independently Verified

Effluent Flowrate = 36,100 l/kkg (8,640 gal/ton)

Constituent	Units	Water & Wastewater Analysis		Gross Effluent Quantity		Net Effluent Quantity	
		Treated Intake	Effluent	Kg/kkg	lbs/ton	Kg/kkg	lbs/ton
pH	-	7.5	8.0-8.5	-	-	-	-
Turbidity	FTU	<1	11	-	-	-	-
Conductivity	$\frac{\mu mhos}{cm}$	966	898	-	-	-	-
TSS	mg/l	11	15	0.54	1.08	0.14	0.29
TDS	mg/l	617	620	22.4	44.8	0.11	0.22
$CaCO_3$ Alkalinity	mg/l	358	323	11.7	23.4	(-1.3)	(-2.6)
$CaCO_3$ Acidity	mg/l	-	-	-	-	-	-
Chloride	mg/l	50	53	1.9	3.8	0.11	0.22
Fluoride	mg/l	0.84	1.01	0.04	0.07	0.0061	0.0122
Sulfate	mg/l SO_4	91.5	90.0	3.2	6.5	(-0.054)	(-0.108)
COD	mg/l	-	6	-	0.2	0.22	0.43
Total Hardness	mg/l	465	468	16.9	33.8	0.11	0.22
Total Phosphate	mg/l PO_4	18.0	22.4	0.8	1.6	0.16	0.32
Ortho Phosphate	mg/l PO_4	15.9	19.3	0.7	1.4	0.12	0.24

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intake so that its discharge responsibility is the net increase in constituent quantities. Plant 159 intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities.

* It is apparent from the "Intake" columns of Tables 11 and 12 that the intake of Plant 159 contains much more dissolved solids (and specifically F, PO_4 and SO_4) than the intake of Plant 028.

* The wastewater quantity per cent of production for Plant 028 is three times that of Plant 159.

The above three differences are interrelated and affect the quantities of fluoride, phosphate and sulfate discharged by Plant 159 because the effluent concentrations are of the same magnitude of the solubilities of the corresponding calcium salts. Hence, the effluent quantities are significantly influenced by factors other than the treatment of the process waters.

The effectiveness of control and treatment techniques used by all four phosphorus plants cited are summarized in Table 13. Plants 028 and 159 achieve very high (97 to 99+%) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents.

In areas of the country where very severe and extended cold weather prevails, total recycle of process water become difficult for two reasons:

1. The return water piping and pumping must be protected against freezing. However, technology such as buried water mains and enclosed, heated pumping stations have been aptly demonstrated in the chemical industry and in water supply operations.

2. The settling ponds may freeze. In a total recycle system, this circumstance would prevent the required water from being supplied back to the process. If an auxiliary fresh water supply were provided to uncouple the process from frequent climatic perturbations, the pond system would have to consist of sufficient holding capacity to prevent temporary overflows and would have to contain sufficient evaporative capacity to prevent long-term accumulation of water.

Both of the above difficulties are formidable but not unyielding to practicable, currently available technology. All aspects of manufacturing including

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TABLE 13 - Summary of Control & Treatment Techniques at Phosphorus-Producing Plants
(For Process Waters Other Than Phossy Water)

	TSS	Total Acidity (Alkalinity)	TDS	Fluoride	Sulfate	Total Phosphate
Raw Waste Loads (from Sec. V)						
Kg/Kkg	42.5	54.5	-	53.5	111	25
lbs/ton	85	109	-	107	222	50
Waste Discharged, Kg/Kkg:						
TVA	0	0	0	0	0	0
Plant 181	0	0	0	0	0	0
Plant 028 (Net)	0.5	1	4	0.1	2	0.2
Plant 159 (Gross)	0.5	(12)	22	0.04	3	0.8
Waste Discharged, lbs/ton:						
TVA	0	0	0	0	0	0
Plant 181	0	0	0	0	0	0
Plant 028 (Net)	1	3	9	0.2	4	0.4
Plant 159 (Gross)	1	(24)	45	0.07	7	1.6
Control & Treatment Efficiency, Per Cent:						
TVA	100	100	100	100	100	100
Plant 181	100	100	100	100	100	100
Plant 028	99	-	-	99+	98	99
Plant 159	99	-	-	99+	97	97

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waste management assume different stances when the chosen environment is far more severe than the norm; however, currently-available technology can cope with environmental challenges of this sort including the special challenges in waste management.

3.1.3 Recommended Level I Guidelines

In view of the existence of three plants (028, 159, and 181) which have already achieved zero discharge of elemental phosphorus; in view of the existence of two plants (TVA and 181) which have already achieved zero discharge of other process waters; in view of the conclusion that "Best Practicable Control Technology Currently Available" is sufficient to achieve zero discharge in other plants (such as Plants 028 and 159); and in full view of the statutory national goal of eliminating the discharge of all pollutants; it is recommended that the Level I effluent guideline be zero discharge.

3.1.4 Wastewater from Ore Washing the Beneficiation

The Level I Guidelines recommended in the previous section do not include wastes from the beneficiation or washing of phosphate rock. This beneficiation is commonly but not exclusively conducted at a separate off-site location. The huge raw waste load from beneficiation, 7.5 Kkg of gangue per Kkg of phosphorus eventually produced, warrants a separate study and separate effluent guidelines.

3.2 The Phosphorus Consuming Segment

3.2.1 Phossy Water

Gross discharges of phossy water are presently avoided by pumping displaced phossy water from the plant's phosphorus storage tank back into the emptying rail car which brought the phosphorus, and by transporting this displaced phossy water to the phosphorus-producing plant for treatment and/or reuse. Such is the practice at Plants 037 and 192.

Smaller quantities of phossy water discharge may also be eliminated through the use of standard engineering techniques. The phosphorus storage tank level control system may be altered to provide an auxiliary water overflow tank with return of the water to the main tank. The avoidance of elemental phosphorus in plant sewer lines can be implemented by more stringent process and operator controls and procedures and by providing traps downstream of reaction vessels.

In view of the extreme toxicity of elemental phosphorus and in view of the available choices from state-of-the-art control techniques, the recommended Level I effluent guideline for phossy water is zero discharge.

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3.2.2 Phosphoric Acid Manufacture

Exemplary Plant 075 operates without the discharge of any process water. There is no fundamental or practical reason why process water should be discharged at all from any dry-process phosphoric acid plant. Minor leaks and spills may be minimized, collected and treated using control techniques generally available and demonstrated in the industry.

The recommended effluent guideline of zero discharge applies generally and with special emphasis upon elemental phosphorus (i.e., phossy water) and upon arsenic residues from the purification of phosphoric acid.

3.2.3 Phosphorus Pentoxide Manufacture

The single raw waste constituent is phosphoric acid from water tail-gas seals. Application of two standard techniques would enable total recycle of this wastewater:

1. Reduction in wastewater quantities by using dilute caustic or lime slurry as tail gas liquor instead of pure water, increasing the absorptive capacity for P_2O_5.

2. Lime treatment and sedimentation to neutralize and to remove the phosphate, permitting total recycle.

In view of the straightforward application of these two techniques, the recommended Level I effluent guideline is zero discharge. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste as estimated in Section V.

3.2.4 Phosphorus Pentasulfide Manufacture

The sole source of process wastewater is the scrubber liquor for fumes from casting liquid P_2S_5. One control technique would be the use of inert-atmosphere casting or vacuum casting to completely eliminate the need for scrubbing. As an alternate to this approach, the application of three standard techniques would permit total recycle of scrubber water:

1. Use of dilute caustic or lime slurry instead of pure water would reduce the wastewater quantities by increasing the absorptive capacity for P_2O_5 and SO_2.

2. Partial recycle of scrubber liquor from a sump would reduce the wastewater quantity by decoupling the buildup of absorbed acids from the mass-transfer requirements for high scrubber flowrates.

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3. Lime treatment and sedimentation to neutralize and to remove phosphate, sulfite and sulfate would permit total recycle.

In view of these different practicable alternates, the recommended Level I effluent guideline is zero discharge. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste load as estimated in Section V.

This guideline also applies to any arsenic-rich residues from the purification of P_2S_5; these solid residues may be properly disposed of by burial as in Plants 147 and 192.

3.2.5 Phosphorus Trichloride Manufacture

The acid wastes from phosphorus trichloride manufacture arise from the hydrolysis of PCl_3 in scrubber water from the reactor/still, from product storage tanks, from product transfering operations and from container cleaning. The scrubber water may be collected in a sump and recycled to decrease the wasted quantity of scrubber water (while still maintaining sufficient scrubber flow rates for effective mass transfer) and to increase the concentrations of waste constituents.

Lime treatment of the wasted water would neutralize the acids and would precipitate the phosphite and phosphate wastes as calcium salts. Subsequent sedimentation in a mechanically-raked clarifier, with the use of a polymeric flocculent, could effectively remove 85 per cent of the suspended solids as a sludge (see Section 3.5.1). This sludge may then be hauled as a slurry for direct landfill, or may be dewatered in sand drying beds or mechanically prior to landfilling. The clarified water may then be discharged, with the following recommended Level I effluent guidelines:

Total Dissolved Solids,	5 Kg/Kkg (10 lbs/ton)
Total Suspended Solids,	0.7 Kg/Kkg (1.4 lbs/ton)
pH,	6 to 10.5

The relaxation of the general pH guidelines to permit high-pH discharges in this case is to allow effective precipitation by an excess of lime. The above quantities of TSS and TDS are based upon the raw waste load as determined in Section V:

HCl,	3 Kg/Kkg (6 lbs/ton)
$H_3PO_3 + H_3PO_4$	2.5 Kg/Kkg (5 lbs/ton)

The soluble $CaCl_2$ resulting from lime-neutralization of HCl is 4.5 Kg/Kkg

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(9 lbs/ton); allowing for some small amount of unprecipitated phosphite and phosphate brings the total dissolved solids to 5 Kg/Kkg (10 lbs/ton). The quantity of precipitated 2 $CaHPO_3 \cdot 3H_2O$, $Ca_3(PO_4)_2$ or 9 $CaO \cdot 3P_2O_5 \cdot Ca(OH)_2$ is dependent upon the relative quantities of these compounds, but is no more than 4.5 Kg/Kkg (9 lbs/ton). With a sedimentation efficiency of 85 per cent, the total suspended solids in the effluent should be no more than 0.7 Kg/Kkg (1.4 lbs/ton).

In the case of PCl_3 manufacture, the soluble chlorides are not removed by the applicable "Best Practicable Control Technology Currently Available", so that the recommended Level I effluent guidelines are not zero discharge. In treating the raw wastes, the total quantity of constituents is not reduced: 5.5 Kg/Kkg (11 lbs/ton) in the raw waste vs. 5.7 Kg/Kkg (11.4 lbs/ton) in the treated effluent. However, the treatment does not remove the toxic acidity, substituting for it residual alkalinity which would be naturally neutralized by carbonation either in receiving streams or in a municipal wastewater treatment plant.

Zero discharge of arsenic-rich reactor/still residues is recommended, since trichloroethylene treatment (as described in Section VII) may be applied.

3.2.6 Phosphorus Oxychloride Manufacture

The types of raw wastes, the types of applicable control and treatment technologies, and the reason for the Level I effluent guidelines not being zero discharge, are all identically parallel for $POCl_3$ manufacture as they are for PCl_3 manufacture. The difference is one of magnitude. For $POCl_3$ manufacture, the raw waste load as determined in Section V is:

HCl,	2 Kg/Kkg (4 lbs/ton)
$H_3PO_3 + H_3PO_4$,	0.5 Kg/Kkg (1 lb/ton)

Using the same rationale as for PCl_3 manufacture, the recommended Level I effluent guidelines are:

Total Dissolved Solids,	3.5 Kg/Kkg (7 lbs/ton)
Total Suspended Solids,	0.15 Kg/Kkg (0.3 lbs/ton)
pH,	6 to 10.5

3.3 The Phosphate Segment

3.3.1 Sodium Tripolyphosphate Manufacture

Exemplary Plant 042 has no process wastes. The dust collected from the spray

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dryer gaseous effluent stream is added to the spray dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray-dryer vent line upstream of the scrubbing operation.

This plant is an excellent example where a combination of in-process controls such as dry dust collection, water reuse, and return to the process of air-borne solids have been utilized to totally avoid any aqueous wastes.

In view of this demonstration, and in view of the general applicability of such techniques throughout the industry, the recommended Level I effluent guideline is zero discharge.

3.3.2 Animal-Feed Grade Calcium Phosphates

Exemplary Plant 182 has no process wastes. Three separate water cycles are used and there is no effluent from any. The acid defluorination scrubber water is neutralized with lime, the solids are settled by ponding, and the pond effluent is reused as scrubber water. The scrubber water for collection of air-borne solids from the reactor and dryer is recirculated with a bleed-off directly into the reactor as process water. Cooling water is recycled through a cooling tower, with the blowdown used as makeup in the solids scrubbing system instead of being wasted. Softened well water is used for cooling water makeup.

This plant is an excellent example where a combination of in-process controls (dry dust collection, recycle of scrubber water to minimize wastewater quantities, return of process waste streams back to the process, and a systems approach towards water use whereby a blowdown stream from one water cycle becomes a makeup stream for another); in combination with a standard lime-treatment, sedimentation and total recycle scrubber water system; results in the discharge of no aqueous wastes.

In view of this demonstration, and in view of the general applicability of such techniques throughout the industry, the recommended Level I guideline is zero discharge.

3.3.3 Food-Grade Calcium Phosphates

The raw aqueous wastes from the manufacture of food-grade calcium phosphates are from two primary and approximately equal sources: the centrate or filtrate from dewatering of the dicalcium phosphate slurry, and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely divided calcium phosphate solids and phosphoric acid from acid units and from excess acid in

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the reaction liquid. The total raw waste load (from Section V) is:

Process Water Wasted,	4,200 l/kkg (1,000 gal/ton)
Total Suspended Solids (2.4%),	100 Kg/kkg (200 lbs/ton)
Phosphoric Acid (0.7%)	30 Kg/kkg (60 lbs/ton)

The first type of currently-available control technology that may be applied is the substitution of dry dust bag collectors for wet scrubbers, as has been done at Plants 003, 042, 119, and 182. The fact that a multi-product plant must provide a separate baghouse for each product does not deny the current availability of this technology but rather increases the cost of such an installation. However, Plant 003, which is a multiple-product, food-grade, calcium phosphates plant, has justified the installation of separate baghouses on the sole basis of profitability from product recovery.

The elimination of wet scrubbing systems would halve the aqueous waste load, so that it would then consist of 2,100 l/kkg (500 gal/ton) containing 2.4 per cent of suspended solids amounting to 50 Kg/kkg (100 lbs/ton) and containing 0.7 per cent of phosphoric acid amounting to 15 Kg/kkg (30 lbs/ton).

Standard lime treatment and sedimentation may then be utilized to neutralize these remaining wastes, to precipitate the phosphate, and to remove a nominal 85 per cent of the suspended solids (with the possible aid of a polymeric flocculent). At a pH of 10.5, the remaining concentration of dissolved solids would be approximately 85 per cent of the original quantity, with the remainder landfilled as sludge. The clarified overflow would then consist of 1,800 l/kkg (430 gal/ton) containing:

Dissolved Solids,	0.0005 Kg/kkg (0.001 lbs/ton)
Suspended Solids,	11 Kg/kkg (22 lbs/ton)

In the case for treatment of PCl_3 and $POCl_3$ wastes, previously discussed in this Section, gravity sedimentation after lime treatment was judged adequate for Level I since the quantity of suspended solids discharged was already much smaller than the quantity of non-removable dissolved solids. In this case for treatment of good-grade calcium phosphate wastes, however, the reverse is true: the great bulk of the wastes discharged after gravity sedimentation is in the form of suspended solids. Hence, it is judged that more extensive treatment should be sought to approach the national goal of eliminating the discharge of all pollutants.

The demonstrated practice at Plant 006, after lime treatment for neutralization and for precipitation of phosphate wastes, is the direct vacuum filtration of

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all of the resulting slurry; a practice adopted when gravity sedimentation was judged inadequate by plant personnel. Vacuum filtration (possibly after conditioning with a polymeric flocculent) can reduce the suspended solids content of the wastewater from phosphates to the level of 0.5 ppm.[30] Based upon these data and upon the level of dissolved phosphates of 0.3 ppm[31], the discharge would contain (on the basis of the total process water wasted, 4,200 l/kkg (1,000 gal/ton)):

Total Dissolved Solids,	0.0015 Kg/kkg (0.003 lb/ton
Total Suspended Solids,	0.0025 Kg/kkg (0.005 lbs/ton)

With the achievement of these extremely low levels of TDS and TSS, or even with considerable relaxation of these levels, the treated-wastewater from the manufacture of food-grade calcium phosphates then is certainly pure enough to be reused as input process water. No product purity restrictions exist any longer which had previously necessitated discharge. In fact, once the commitment towards total recycle is made, the lime treatment step may be by-passed since the ionic species from the dissolved solids and the phosphoric acid are precisely those desired in the reaction vessel.

Since the above rationale is entirely based upon demonstrated, currently-available treatment technology, the recommended Level I effluent guidelines is zero discharge.

4.0 Summary of Level I Recommended Guidelines for Process Water

4.1 Zero Discharge

The recommended Level I guidelines for process water is zero discharge for the manufacture of the following chemicals:

Phosphorus (and Ferrophosphorus)
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Sodium Tripolyphosphate
Calcium Phosphate (Food Grade)
Calcium Phosphates (Animal Feed Grade)

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4.2 Permitted Discharges

The recommended Level I guidelines for process water for the manufacture of PCl_3 and $POCl_3$ are:

	Phosphorus Trichloride	Phosphorus Oxychloride
Total Suspended Solids:		
Kg/kkg	0.7	0.15
lbs/ton	1.4	0.3
Total Dissolved Solids:		
Kg/kkg	5	3.5
lbs/ton	10	7
pH	6-10.5	6-10.5

The above guidelines apply to monthly average values.

Additional restrictions of these discharges would be:

1. Zero elemental phosphorus discharged.
2. Arsenic compounds permitted only at the naturally-occurring level in the discharged phosphorus compounds. Under no circumstances is the discharge of arsenic compounds permitted when they exist in an enriched state (i.e., as residues from the purification of phosphorus compounds).
3. No discharge of other heavy metals or of toxic materials is permitted.

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SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE, LEVEL II EFFORT GUIDELINES AND LIMITATIONS

1.0 INTRODUCTION

The effluent limitations which must be achieved by July 1, 1983 are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the non-fertilizer phosphorus chemicals industry, this level of technology was based on the very best control and treatment technology employed by a specific point source within the industrial category or subcategory, or where it is readily transferable from one industry process to another. Level II technology places equal emphasis upon in-process controls as upon control or treatment techniques employed at the end of a production process.

Those plant processes and control technologies which at the pilot plant, semi-works, or other level, have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities were also considered in assessing Level II technology. Level II is the highest degree of control technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and including "no discharge" of pollutants. Although economic factors are considered in this development, the costs for this level of control are intended to be for the top-of-the-line of current technology subject to limitations imposed by economic and engineering feasibility. However, Level II may be characterized by some technical risk with respect to performance and with respect to certainty of costs. Therefore, Level II may necessitate some industrially-sponsored development work prior to its application.

The following factors were taken into consideration in determining Level II technology:

a. The age of equipment and facilities involved;

b. the process employed;

c. the engineering aspects of the application of various types of control techniques;

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d. process changes;

e. cost of achieving the effluent reduction resulting from application of Level II technology; and

f. non-water quality environmental impact (including energy requirements).

2.0 GUIDELINES FOR NON-CONTACT COOLING WATERS AND BLOWDOWNS

The Level II guidelines are the same as for Level I except that monitoring shall be required for process leaks and provisions shall be made for emergency holding facilities for cooling water contaminated by leaks until such time as they can be treated.

3.0 PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gaseous, airborne, or solid wastes. All values of guidelines and limitations presented below for total dissolved solids (TDS), total suspended solids (TSS), heavy metals and toxic pollutants and other parameters are expressed as monthly averages in units of pounds of parameter per ton and kilograms of parameter per metric ton of product produced except where expressed as a concentration. Where zeros appear for a parameter when there is discharge of process wastewater, the zero means no increase above that of the intake or receiving water whichever is lower. Zero discharge of process wastewater means that no process water be discharged from the plant into surrounding waterways.

Based upon the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best available control technology economically achievable in the various categories of the non-fertilizer phosphorus chemicals industry.

3.1 All Chemicals Except Phosphorus Trichloride and Phosphorus Oxychloride

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The recommended Level II guidelines for process water are the same as the Level I guidelines, i.e., zero discharge, for the manufacture of the following chemicals:

Phosphorus (and Ferrophosphorus)
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Sodium Tripolyphosphate
Calcium Phosphates (Food-Grade)
Calcium Phosphates (Animal-Feed Grade)

3.2 Manufacture of Phosphorus Trichloride and Phosphorus Oxychloride

3.2.1 In-Process Controls

The largest contribution to the raw waste load from these processes is from the escape of PCl_3 vapor from the reactor/stills. The method for drastically reducing this contribution is clear-cut: the substitution of refrigerated condensers for water-cooled condensers (or the addition of refrigerated condensers downstream of water-cooled condensers). Refrigerated condensers are already in use at Plant 037 in the manufacture of $POCl_3$ by the air-oxidation process.

As an added step, a demister can be added downstream of the refrigerated condenser to prevent condensed but dispersed PCl_3 from escaping to the scrubber. One concept for this demister is a short section of column packed with metal packing (for good heat transfer) within the refrigerated condenser.

As a corollary to this principle, other sources of PCl_3 and $POCl_3$ vapors could be controlled by refrigerated condensers or cold traps. The storage tank vent and vents for the transfer of liquid product are included in this concept. Alternately, the liquid products could be maintained at low temperatures by refrigerating coils in the storage tanks, so that vapors from storage and transfer would be minimized.

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In view of the order-of-magnitude or greater reduction in the vapor pressure of these products resulting from readily-available refrigeration levels, plus the effect on PCl_3 condensation from doubling (or more) the temperature driving force for heat transfer, a reasonable expectation is that the PCl_3 vapor (and mist) losses could be cut to 10 per cent of the present values.

The acid wastes from washing tank cars and tank trucks, and from washing used $POCl_3$ filter elements, are very small at present. Water use data taken from Plant 037, supplemented by independent analyses of the wastewater, yielded the results in Table 14. The total raw waste generated in truck-loading, in tank-car cleaning, and in filter-element washing is 0.014 kg/kkg (0.028 lbs/ton) of HCl plus 0.003 kg/kkg (0.007 lbs/ton) of total phosphates; very small fractions of the total raw waste load as discussed in Section V.

The wastes from washing returnable nickel drums, however, is estimated to be much larger. Should this raw waste indeed prove significant, the returnable container usage could be abandoned in favor of non-returnable epoxy-lined drums (as is the partial practice at Plant 147 for PCl_3).

Another minor source of wastes is the generation of HCl (not PCl_3) from the reactor/stills, resulting from small quantities of stray moisture in the vessels. The HCl is driven off as a non-condensible while the corresponding H_3PO_3 and H_3PO_4 is retained as reactor residue.

All in all, the above-outlined in-process control techniques could drastically reduce the raw waste load to perhaps 10 per cent of the original value, so that the estimated raw waste quantities would then become (for either PCl_3 of $POCl_3$ manufacture):

HCl,	0.3 kg/kkg (0.6 lbs/ton)
$H_3PO_3 + H_3PO_4$,	0.25 kg/kkg (0.5 lbs/ton)

As important as the reduction in the wastewater constituent quantities would be a corresponding reduction in the quantity of wastewater generated. Tail-gas scrubbers should be very much smaller and should require much lower water flowrates.

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TABLE 14

Minor Wastes from Plant 037 (PCl_3 and $POCl_3$)

	Truck-Loading Vent Scrubber	Tank Car Cleanout Water	Filter Element Washout Drum
Water Use: l/kkg	8.8	10.5	0.46
gal/ton	2.1	2.5	0.11
Constituent Analysis, ppm:			
Chloride	340	715	6,480
Total PO_4	260	26	590
Total Acidity	660	-	18,200
Raw Waste Load, kg/kkg:			
Chloride	0.0030	0.0075	0.0030
Total PO_4	0.0023	0.0003	0.0003
Total Acidity	0.0058	--	0.0083
Raw Waste Load, lbs/ton:			
Chloride	0.006	0.015	0.006
Total PO_4	0.005	0.001	0.001
Total Acidity	0.012	--	0.017

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As an added step, the scrubber water could be recycled from a sump, thereby decoupling the wastewater quantity (blowdown from the sump) from the mass-transfer requirements for scrubbing. Furthermore, water use could be cascaded in the plant, with (for example), the wastewater from tank car washing being used as makeup in the tail-gas scrubber system.

3.2.2 End of Process Treatment

At the new low levels of wastewater flowrates and constituent quantities, simple lime neutralization of moderate pH (without sedimentation) would result in the following wastewater characteristics:

Wastewater Quantity,	500 l/kkg (120 gal/ton)
Total Dissolved Solids,	0.5 kg/kkg (1.0 lbs/ton)
Total Suspended Solids,	0.35 kg/kkg (0.7 lbs/ton)
pH,	6 - 9

Further lime neutralization and removal of suspended solids would not appreciably reduce the quantity of total dissolved solids, and would trade off reduction in total suspended solids for higher pH levels.

At this point, the wastewater quantity would be extremely low, and a practicable final step would be evaporation to dryness. An idea of the costs of evaporation can be obtained by assuming a plant manufacturing 59 kkg/day (65 tons/day) of total PCl_3 and $POCl_3$. The wastewater quantity would be 30,000 l/day (7,800 gal/day). Using the data of Section VIII - 3.5.3 for single-effect evaporation,

Capital Cost = $6,700

Annual Costs:		
	Capital Recovery	= $ 1,600
	Taxes & Insurance	= 300
	Operation & Maintenance	= 14,700
		$16,600

Unit Cost = $0.85/kkg ($0.77/ton)

This unit cost is only 0.3 per cent of the current selling price, $295/kkg ($268/ton).

It is entirely possible that a rigorous economic evaluation might result in a decision to dispose of the original raw waste load by

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evaporation, rather than to bear the expense of the in-process controls discussed above which minimize (but do not eliminate) the waste. The wastewater quantity to be evaporated would be the original quantity, 5,000 l/kkg (1,200 gal/ton), or 300,000 l/day (78,000 gal/day); and the costs would be:

Capital Cost =	$38,400	
Annual Costs:	Capital Recovery	= 8,900
	Taxes & Insurance	= 1,900
	Operation & Maintenance	= 147,000
Unit Cost = $8.10/kkg ($7.35/ton)		

Using the most conservative approach, i.e., to evaporate all of the wastewater without any in-process control to reduce its quantity, would cost 2.8 per cent of the current selling price. The fundamental reason is that despite the high unit cost of evaporating water, the wastewater quantities for PCl_3 and $POCl_3$ are very small. The conclusion is reached that the application of this available technology is economically achievable.

The final step of total evaporation would bring the PCl_3 and $POCl_3$ manufacturing processes into line with the rest of the non-ferilizer phosphorus chemicals industry by achieving the national goal of eliminating the discharge of all pollutants.

It is therefore recommended that the Level II guidelines for PCl_3 and $POCl_3$ manufacture be zero discharge.

NOTICE: THESE ARE TENTATIVE RECOMMENDATIONS BASED UPON INFORMATION IN THIS REPORT AND ARE SUBJECT TO CHANGE BASED UPON COMMENTS RECEIVED AND FURTHER INTERNAL REVIEW BY EPA.

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SECTION XI

NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT STANDARDS LEVEL III GUIDELINES AND LIMITATIONS

1.0 INTRODUCTION

This level of technology is to be achieved by new sources. The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance". Level III technology was to be evaluated by adding to the consideration underlying the identification of Level II technology a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process control technology, identified in Level II, Level III technology was to be based upon an analysis of how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods or other alternatives were to be considered. However, the end result of the analysis identifies effluent standards which would reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination which was to be made for Level III technology is whether a standard permitting no discharge of pollutants is practicable.

The following factors were to be considered with respect to production processes which were analyzed in assessing Level III technology:

a. the type of process employed and process changes;

b. operating methods;

c. batch as opposed to continuous operations;

d. use of alternative raw materials and mixes of raw materials;

e. use of dry rather than wet processes (including substitution of recoverable solvents for water); and

f. recovery of pollutants as by-products.

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2.0 GUIDELINES FOR NON-CONTACT COOLING WATERS AND BLOWDOWNS

The Level III guidelines are the same as for Level II.

3.0 PROCESS WATER GUIDELINES

Based upon the information contained in Sections III through X of this report, the following determinations were made on the degree of effluent reduction attainable with the application of new source standards for the various categories of the non-fertilizer phosphorus chemicals industry.

Since the Level II guidelines for all of the chemicals considered in this study of the non-fertilizer phosphorus chemicals industry were zero discharge, the recommended Level III guidelines are identical to the Level II guidelines.

4.0 PRETREATMENT STANDARDS

In addition to the recommendation of Level III technology and related effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant which would interfere with, pass through, or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter wastewater treatment plant were identified. A determination was made of whether the introduction of such pollutants into the treatment plant should be completely prohibited.

4.1 Wastewater Flowrate

A determination must be made on an individual basis about the impact of a plant's discharge upon the total hydraulic capacity of both the municipal collection system and the municipal wastewater treatment plant. At an extreme, hydraulic overloading will result in overflows or bypasses as the capacities of pumping stations (both in the collection system and the raw wastewater pumping stations at the treatment plant) are exceeded. It must be remembered that an overflow of combined industrial/municipal wastewater has the same adverse environmental effect as an overflow of raw domestic sewage. At a minimum, hydraulic overloading would result in reduced efficiency of the treatment plant because:

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* Primary and secondary clarifiers would be operating at excessive overflow rates.
* Secondary treatment units (activated sludge or trickling filter) would be operating at a food deficiency since the wastewater from the phosphorus chemicals industry would provide no organic material.
* Trickling filters would become flooded (and so anaerobic).
* Grit chambers would have a high linear velocity resulting in the carry-over of grit and the subsequent adverse effects on equipment.
* The capacity of air blowers for activated sludge secondary treatment may be exceeded, resulting in reduced levels of dissolved oxygen.
* The capacity of chlorinators may be exceeded, resulting in insufficient disinfection.
* The critical operating parameters of the activated sludge unit may be compromised.

The domestic wastewater flowrate follows a well-known diurnal cycle; if the industrial contribution could be staggered to provide flow equalization, the impact of the added flowrate could be minimized. Conversely, sporatic slug discharges could make periodic overloading more probable.

It is recommended that each source of wastewater from the non-fertilizer phosphorus chemicals industry be required to provide an analysis of the impact of its flow contribution upon the hydraulic capacity of the publicly-owned collection and treatment system, should it desire to use the public system. This analysis should include the effects of time-varying flowrate.

4.2 Suspended Inorganic Solids

High concentrations of suspended inorganic solids might overload the primary sludge collectors, the primary sludge pumps, the sludge thickener, the sludge dewatering operation, and the sludge disposal system. In addition, since these solids provide no organic food for secondary treatment organisms, they would reduce the active biological-solids fraction (i.e., reduce the mixed liquor volatile suspended solids), thereby reducing the efficiency of secondary treatment.

It is recommended that the maximum concentration of suspended inorganic solids be set at 250 mg/l; equivalent to the maximum concentrations normally found in domestic wastewaters.

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4.3 Acidity

While moderate alkalinity may be tolerated since carbon dioxide produced in secondary treatment by the microbial oxidation of organic material will provide neutralization; free mineral acidity normally cannot be tolerated by the organisms in the secondary treatment biomass. The proteins in these organisms are precipitated and coagulated at pH 4 to 5. (44)

Another strong reason for avoiding acidic contributions to publicly-owned treatment plants is that acidic wastes would drastically promote corrosion of equipment.

It is recommended that the allowable pH range be set at 6 to 10.5.

4.4 Dissolved Inorganic Solids

Dissolved inorganic solids would pass through a secondary wastewater treatment plant without being removed. Hence, reliance upon publicly-owned treatment plants would be no treatment at all with respect to dissolved solids, and it would be equivalent to direct discharge.

It is recommended that the pretreatment standards for dissolved inorganic solids be the same as the applicable Levels I, II, or III effluent limitation guidelines.

4.5 Heavy Metals or Toxic Materials

Heavy metals or toxic materials (including elemental phosphorus and enriched arsenic compounds) would at best, pass through a publicly-owned treatment plant, and at worst, adversely affect the microorganisms in secondary treatment.

It is recommended that the pretreatment standards for heavy metals or toxic materials be zero discharge.

4,6 Dissolved Phosphates

While dissolved phosphates would generally pass through secondary treatment plants with the wastewater treatment plant effluent, they would affect the sludge operations. Gravity-thickened sludge (6 to 12 per cent solids) is normally conditioned with lime, ferric chloride, or alum prior to dewatering operations, although polymeric flocculents are also widely used. The phosphates would be precipitated as the calcium, ferric, or aluminum phosphate and would thus render the conditioning step ineffective by partially or totally removing the active cation from solution.

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A similar situation exists in tertiary treatment, in the phosphate-removal step using lime, ferric chloride, or alum. In this case, the chemical requirements would be increased and the sludge handling capacity of the treatment plant could be overloaded. While these pretreatment standards apply only to secondary plants, precautions should be taken to avoid adverse effects when tertiary treatment might be added in future years.

It is recommended that the maximum permissible phosphate concentration be set at 30 mg/l; equivalent to the maximum concentrations normally found in domestic wastewaters.(31)

4.7 Summary of Recommended Pretreatment Standards

It is recommended that wastewaters discharged from plants in the phosphorus chemicals industry into publicly-owned wastewater collection and treatment systems conform to the following limitations:

1. An impact analysis of the wastewater flowrate (including time-varying effects) upon the hydraulic capacity of the public treatment plant be provided by the phosphorus chemicals plant.

2. The maximum amounts of total dissolved solids be the same as the applicable Levels I, II, or III effluent limitation guidelines.

3. The pH mus be between 6 and 10.5.

4. Zero contribution of heavy metals and toxic materials.

5. The maximum concentration of total suspended solids be 250 mg/l.

6. The maximum concentration of total phosphate (as PO_4) be 30 mg/l.

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SECTION XII

ACKNOWLEDGMENTS

The preparation of this report was accomplished through the efforts of the staff of General Technologies Corporation under the direction of Dr. R. G. Shaver. Mr. Donald H. Sargent was the Principal Investigator for the project. The following individuals of the Staff of General Technologies Corporation made significant contributions to this effort:

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SECTION XIII

REFERENCES

1. Current Industrial Reports, Inorganic Chemicals, U. S. Bureau of Census, Series M28A(71)-14.

2. Private Communication.

3. Study of the Economic Impact of the Cost of Alternative Federal Water Quality Standards on Ten Inorganic Chemicals, U. S. Environmental Protection Agency, Washington, D.C. Dec. 4, 1972.

4. G. S. G. Beveridge and R. G. Hill, Phosphoric Acid Process Survey, Chem & Process Eng. 49, July 1968, p. 61-6,73 (Part I), Aug 1968, p.63-70 (Part II), 305 References in Bibliography.

5. J. C. Barber, Waste Effluent; Treatment and Reuse, Chem Eng Progress 65, 6, 70-3 (June 1969).

6. J. C. Barber, The Cost of Pollution Control, Chem. Eng Progress 64, 9, 78-82 (Sept 1968).

7. J. C. Barber and T. D. Farr, Fluoride Recovery from Phosphorus Production, Chem Eng Progress 66, 11, 56-62 (Nov 1970).

8. R. E. LeMay and J. K. Metcalf, Safe Handling of Phosphorus, Chem Eng Progress 60, 12, 69-73 (Dec 1964).

9. P. Ellwood, Electric-Furnace Phosphorus, Chem Eng 72, 54-6 (Feb 1, 1965).

10. H. S. Bryant, N. G. Holloway and A. D. Silber, Phosphorus Plant Design-New Trends, Ind & Eng Chem 62, 4, 9-23 (April 1970).

11. W. A. Faith, D. B. Keyes, and R. L. Clark, Industrial Chemicals, 3rd ed., Wiley, N.Y. (1965).

12. R. E. Kirk and D. F. Othmer, Encyclopedia of Chemical Technology, Interscience, N.Y. (1966).

13. R. N. Shreve, Chemical Process Industries, McGraw-Hill, N.Y. (1967).

14. S. H. Stow, Occurrence of arsenic and the color-causing components in Florida land-pebble phosphate rock, Economic Geology 64, 667-71 (Seot 1969), Discussion, 65, 64-6 (Jan. 1970).

15. Existing Practice or Data taken at Plant No. 003.

16. " " " " " " " " 006.

17. " " " " " " " " 028.

18. " " " " " " " " 037.

19. " " " " " " " " 042.

20. " " " " " " " " 075.

21. " " " " " " " " 119.

22. " " " " " " " " 147.

23. " " " " " " " " 159.

24. " " " " " " " " 181.

25. " " " " " " " " 182.

26. " " " " " " " " 192.

27. N. A. Lange, Handbook of Chemistry, 10th ed, McGraw-Hill, N.Y. (1961).

28. D. G. Downing, R. Kunin and F. X. Poilliot, "Desal Process -- Economic Ion Exchange System for Treating Brackish and Acid Mine Drainage Waters and Sewage Waste Effluents", Water-1968, Chem. Eng. Prog. Symposium 90, Vol. 64, 1968.

29. R. C. Weast (ed.), Handbook of Chemistry and Physics, 52nd edition, The Chemical Rubber Co, Cleveland (1971-1972).

30. B. J. Sevey, R. B. Hudson, R. A. Capeil, R. A. Rose, Soluble Phosphate Recovery at Monsanto's Trenton, Michigan Plant, 42nd Annual Conference of the Water Pollution Control Federation, Dallas, Texas, Oct. 6, 1969.

31. Black & Veatch, Consulting Engineers, Process Design Manual for Phosphorus Removal, U. S. Environmental Protection Agency Program 17010 GNP, Contract 14-12-936 (October 1971).

32. B. L. Goodman and K. A. Mikkelson, Advanced Wastewater Treatment, Chem Eng Deskbook Issues, April 27, 1970, p 75-83.

33. T. J. Tofflemire and L. J. Hetling, Treatment of a Combined Wastewater by the Low-Lime Process, J. WPCF 45, 2, 210-20. (Feb 1973).

34. Anon., Phosphate Users Regroup, Chemical Engineering, August 10, 1970, p.66.

35. Anon., Chem Eng., Sept. 7, 1970, p.40.

36. L. L. Ames and R. B. Dean, Phosphorus Removal from Effluents in Alumina Columns, JWPCF 42, 5, Pt 2, R 161-72 (May 1970).

37. B. W. Dickerson and P. J. Farrell, Lab and Pilot-Plant Studies on Phosphate Removal from Industrial Wastewater, JWPCF 41, 1, 59-62 (Jan. 1969).

38. O. E. Albertson and R. J. Sherwood, Phosphate Extraction Process, JWPCF 41, 1469 (1969).

39. R. G. Schussler, Phosphorus Removal: A Controllable Process, CEP Symp. Ser. 67, 107, 536-40 (1971).

40. A. Shindala, Evaluation of Current Techniques for Nutrient Removal from Wastewaters, Water Resources Bulletin 8, 5, 987-1005 (Oct 1972).

41. Anon., Sorption Wins Phosphoric Acid from Finishing Wastes, Chem Eng 79, 60 (June 1972).

42. R. F. Waters, Recovery of Metals and Phosphates from Waste Phosphate Sludge, Metal Finishing 69, 39-42 (Aug 1971).

43. Anon, Phosphate-Plant Waste Looms as Hydrofluoric-Acid Source, Chem Eng, May 4, 1970, p.46-48.

44. M. M. Ellis, Detection and Measurement of Stream Pollution, in Biology of Water Pollution, U. S. Dept. of the Interior, FWPCA (1967).

45. Hearings before the Senate Subcommittee on Air and Water Pollution, 92nd Congress, 1st Session, June 8, 1970, U. S. Govt. Printing Office 44-393 (Parts 4 and 5).

46. Ibid, Part 4, p. 1378-1502, The Eutrophication Problem: A Review and Critical Analysis (FMC Corporation)

47. Ibid, Part 5, p. 1899-.912, Hazards of Arsenic in the Environment, With Particular Reference to the Aquatic Environment (Federal Water Quality Administration).

48. F. A. Patty (ed.), Industrial Hygiene and Toxicology, Vol. II-Toxicology, 2nd revised edition, Interscience, N.Y. (1962).

49. The National Estuarine Pollution Study, Report of the Secretary of the Interior to the U. S. Congress, 91st Congress, 2nd Session, U.S. Senate Document No. 91-58.

50. G. Power, Chesapeake Bay in Legal Prospective, U. S. Dept. of the Interior, FWPCA (March 1970).

51. Joint Hearings on the National Environmental Policy Act before the U. S. Senate Committee on Public Works and the Committee on Interior and Insular Affairs, 92nd Congress, 2nd Session, Serial No. 92-H32 (March 1972).

52. Anon., Detergent Enzymes, Arsenic Pose Health Problems, C & E News 48, 13-14 (Feb. 23, 1970).

53. E. E. Angino et. al., Arsenic in Detergents: Possible Danger and Pollution Hazard, Science 168, 389-90 (April 17, 1970); Discussion 170, 870-2 (Nov. 20, 1970).

54. D. E. Aiken and E. H. Byard, Histologic Changes in Lobsters Exposed to Yellow Phosphorus, Science 176, 1434-5 (June 30, 1972).

55. J. R. Goldsmith et. al., Evaluation of Health Implications of Elevated Arsenic in Well Water, Water Res. 6, 1133-6 (Oct. 1972).

56. W. F. Johnson and E. Hinden, Bioconcentration of Arsenic by Activated Sludge Biomass, Water & Sewage Works 119, 95-7 (Oct. 1972).

57. Anon., No Danger from Arsenic, C & E News, 49, 8 (Sept 6, 1971).

58. W. W. Eckenfelder,Jr. and D. L. Ford, Economics of Wastewater Treatment, Chem Eng 76, 109-18 (Aug 25, 1969).

59. Y. Maystre and J. C. Geyer, Charges for Treating Industrial Wastewater in Municipal Plants, J. W.P.C.F. 42, 1277-91.

60. W. W. Eckenfelder, Jr. and C. E. Adams, Jr., Design and Economics of Joint Wastewater Treatment, ASCE Proc. 98 (SAI, no. 8746), 153-67 (Feb. 1972). Discussion, 98 (SAI, no. 9225), 804-5 (Oct. 1972).

61. W. W. Eckenfelder, Jr. and J. L. Barnard, Treatment-Cost Relationship for Industrial Wastes, CEP 67, 76-85 (Sept 1971).

62. P. E. Robinson and F. P. Coughlan, Jr., Municipal-Industrial Waste Treatment Costs, Tappi 54, 2005-10 (Dec 1971).

63. R. J. Bender, Solid Waste Disposal in Chemical Plants, Power 111, 65 (March 1967).

64. G. L. Chiagouris, Analyzing the Cost of Solid Waste Disposal, Plant Engineering 26, 82-5 (March 23, 1972).

65. G. A. Sawyer, New Trends in Wastewater Treatment and Recycle, Chem Eng, July 24, 1972, p. 120-9.

66. J. C. Sonnichsew, Jr., et. al., Cooling Ponds - A Survey of the State of the Art, Hanford Engineering Development Laboratory, Report HEDL-TME-72-101 (Sept 1972).

67. Private communications from E. I. duPont (May 3 and 16, 1973).

68. J. Kumar, Selecting and Installing Synthetic Pond Linings, Chem Eng, p. 67-8 (Feb 5, 1973).

69. P. M. Rapier, Ultimate Disposal of Brines from Municipal Wastewater Renovation, CEP Sym. Series 107, 67, 340-51.

70. Private Communication from EIMCO Division, Enviro-Tech Corp., Salt Lake City, Utah.

71. Private Communication from Dorr-Oliver Co., Stamford, Conn.

SECTION XIV

GLOSSARY

Barn

A room-like condensation chamber for anhydrous phosphorus pentoxide.

Burden

The combined rock, coke and silica feed to a phosphorus electric furnace.

DCP

Dicalcium Phosphate Dihydrate, $CaHPO_4 \cdot 2H_2O$

Dry Process Phosphoric Acid

Phosphoric acid made from elemental phosphorus. Also called furnace acid.

Furnace Acid

Phosphoric acid made from elemental phosphorus. Also called dry process phosphoric acid.

MCP

Monocalcium Phosphate Monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$

Nodule

Semi-fused agglomerated and calcined phosphate rock particle.

Phosphorus Mud

Sludge or emulsion of phosphorus, dust, and water.

Phossy Water

Water containing colloidal phosphorus.

STP

Sodium Tripolyphosphate, $Na_5P_3O_{10}$

TCP

Tricalcium Phosphate, $Ca_3(PO_4)_2$

Wet Process Phosphoric Acid

Phosphoric acid made from phosphate rock and sulfuric acid.

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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMTATIONS GUIDELINES AND STANDARDS OF PERFORMANCE

NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

ERRATA SHEETS

PREPARED BY

GENERAL TECHNOLOGIES CORPORATION
FOR THE
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

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ABSTRACT

A study was made of the non-fertilizer phosphorus chemicals industry by the General Technologies Corporation for the Environmental Protection Agency, for the purpose of developing effluent limitation guidelines, Federal standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act Amendments of 1972.

For the purpose of this study, the non-fertilizer phosphorus chemicals industry was defined as the manufacture of the following chemicals: phorphorus (and by-product ferrophosphorus), phosphoric acid (dry process only), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, phosphorus oxychloride, sodium tripolyphosphate and the calcium phosphates.

Effluent limitation guidelines were developed as a result of this study, defining the degree of effluent reduction attainable through the application of:

Level I, the best practicable control technology currently available (BPCTCA), and

Level II, the best available technology economically achievable (BATEA).

The Level I and Level II degrees of effluent reduction must by law be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively.

Level III, the standards of performance for new sources, was also defined; as were the pretreatment requirements with respect to municipal treatment of the industry's wastewaters.

Except for PCl_3 and $POCl_3$ manufacture, the recommended Level I guideline for the entire industry was zero discharge of process water. The quantitative limitations upon each type of pollution parameter permitted for PCl_3 and $POCl_3$ manufacturing discharges were defined; they are basically the remaining constituents after wastewater neutralization and removal of suspended solids. No harmful materials may be discharged.

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For Level II, application of the best available technologies for treating dissolved solids would enable the PCl3 and POCl3 manufacturing operations to achieve zero discharge. Upon judgment that this would be economically achievable, the recommendation was made that the Level II (and Level III) guideline be zero discharge of all process water from the entire industry.

The recommendation for non-contact cooling water discharges is that they be permitted for Levels I, II and III providing they meet specific conditions restricting their damage to the environment and providing for emergency procedures in the event of their contamination.

The recommendation for pertreatment standards specifically covers flowrate, total suspended solids, total dissolved solids, total phosphate, pH, metals, and harmful materials.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the non-fertilizer phosphorus chemicals industry was divided into the phosphorus production segment, the phosphorus-consuming segment, and the phosphates segment.

The phosphorus-production segment of the industry is characterized by large quantities of raw process wastes, including highly deleterious phossy water and highly-acidic scrubber and quenching wastewaters, both containing large quantities of fluorides, other dissolved solids, and suspended solids. Through a combination of in-process controls and end-of-process treatment, several plants within this segment have achieved zero discharge of phossy water, two have achieved zero discharge of other process wastewaters, and one has achieved zero discharge of any wastewater. While other plants now demonstrate abatement practices resulting in 97 per cent or greater reduction in the raw waste load before discharge, the total recycle of process water without any discharge has been aptly demonstrated using the best practicable control technology.

The phorphorus-consuming segment of the industry is charac-. terized by the absence of direct process wastewater; the chemicals produced are readily hydrolyzed so that the processes are essentially dry. However, just because the products are readily hydrolyzed, water is universally used for air-pollution abatement scrubbing of tail gases, for periodic cleaning of reaction vessels, and for the general washing of shipped containers; all resulting in acidic wastewaters. In addition, water is used in protecting and transferring the raw material, elemental phosphorus, and phossy water is therefore a raw waste from this segment. Except for the manufacture of dry-process phosphoric acid (where in-process control has been demonstrated to achieve zero discharge of aqueous wastes), this segment has not yet achieved sufficient reduction of effluents. The application, however, of currently-available technology is shown by this study to permit total recycle of wastewaters (and so zero discharge) for the manufacture of P_2O_5 and P_2S_5; and to achieve the neutralization and removal of most suspended solids prior to discharge for the manufacture of PCl_3 and $POCl_3$.

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The above guidelines apply to monthly average values. The maximum values for daily averages ot total suspended solids and total dissolved solids are twice the monthly average values. The daily average pH limitation is the same as the monthly average limitation. Additional restrictions upon the discharges are:

1. Zero elemental phosphorus discharged.
2. Arsenic compounds permitted only at the naturally-occuring level in the discharged phosphorus compounds. Under no circumstances is the discharge of arsenic compounds permitted when they exist in an enriched state (i.e., as residues from the purification of phosphorus compounds).
3. No discharge of other heavy metals or of harmful materials is permitted.

The recommendations for cooling water and blowdown discharges are:

Level I

An allowed discharge of all non-contact cooling waters provided that the following conditions are met:

(1) No harmful or hazardous pollutants are added. Cooling waters discharged must not have levels of chromate, zinc, or other harmful pollutants higher than that of the intake water or receiving water, whichever is lower.
(2) Thermal pollution be in accordance with Environmental Protection Agency policy.
(3) All non-contact cooling waters should be monitored to detect leaks from the process and provisions should be made for emergency treatment prior to release.
(4) No untreated process waters be added to the cooling waters prior to discharge.

An allowed discharge of water treatment, cooling tower and boiler blowdowns provided these do not contain deleterious or otherwise hazardous materials such as chromium or cadmium and are within the required pH range of 6 to 9 as measured both as a daily average and a monthly average.

Levels II and III

The same as Level I except that monitoring shall be required for process leaks and provisions made for emergency holding facilities for cooling water contaminated by leaks until such time as they can be treated.

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ommended pretreatment standards are:

1. An impact analysis of the wastewater flowrate (including time-varying effects) upon the hydraulic capacity of the public treatment plant be provided by the phosphorus chemicals plant.
2. The maximum amounts of total dissolved solids be the same as the applicable Levels I, II, or III effluent limitation guidelines.
3. The pH must be between 6 and 10.5.
4. Zero contribution of metals and harmful materials.
5. The maximum concentration of total suspended solids be 250 mg/l.
6. The maximum concentration of total phosphate (as PO4) be 30 mg/l.

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SECTION IV

INDUSTRY CATEGORIZATION

1.0 SEGMENTS OF THE INDUSTRY

For the purpose of waste treatment and effluent limitations, the non-fertilizer phosphorus chemicals industry may be divided into three discrete segments, which coincide with a breakdown of the industry according to the flow of materials as outlined in Section III. Other factors were not deemed important in categorization (see subsection 3.0).

1.1 The Phosphorus Production Segment

Phosphorus (and by-product ferrophosphorus) production stands by itself as a smelting operation, as opposed to more conventional chemical processes. In phosphorus production, a grossly impure raw material is involved, and raw wastes and by-products are generated which dwarf the quantities of the primary product. The remainder of the industry starts with relatively pure materials, waste streams are consequently much smaller.

1.2 The Phosphorus Consuming Segment

The chemicals that are made directly from elemental phosphorus (phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide and phosphorus trichloride) may also be grouped because aqueous wastes arise primarily from sources other than the direct process stream. Air pollution abatement unit operations, product purification residues, tail-gas seals, vessel cleanings, and leaks and spills are the sources of the aqueous waste streams. Phosphorus oxychloride has been added to this segment despite the fact that phosphorus is not a direct raw material of its production; however, the waste streams have similar origins.

1.3 The Phosphate Segment

The chemicals that are made from phosphoric acid (sodium tripolyphosphate and the calcium phosphates) constitute a separate segment because excess process water is used in their manufacture, and also because they are finely-divided solid products. The former characteristic gives rise to some aqueous wastes of direct process origin; the latter characteristic gives rise to aqueous wastes from wet dust scrubbing equipment.

Wet process phosphoric acid contains approximately one percent fluoride in various forms. The defluorination consists of treating the heated acid with finely-divided silica and steaming or aerating, which liberates silicon tetrafluoride gas:

$$SiO2 + 4HF \rightarrow SiF4 + 2H2O$$

Wet scrubbers then hydrolyze and collect this gas as fluosilicic acid and silicic acid:

$$3\ SiF4 + 3H2O \rightarrow 2H2SiF6 + H2SiO3$$

The hot defluorinated phosphoric acid is then charged to the reactor to make dicalcium phosphate.

3.0 OTHER FACTORS CONSIDERED

Factors such as age of plant, size of plant, geographical location, product purity and waste control technologies do not generally justify further segmentation of the industry. Similarities in waste loads within the categories and the availability of treatment and control technologies also substantiate this. Water use is determined by the needs of the individual plant and is primarily determined by the availability and quality of water supply sources and the degree of water recycling employed in the specific process, so that water usage also does not lend itself to categorization.

TABLE 4

Composition of Commercial Phosphate Rocks

Expressed as kg per kkg (lbs/ton) of Phosphorus Produced

Sources: 1. R. E. Kirk and D. F. Othmer, Encyclopedia of Chemical Technology, Interscience, N.Y. (1966), Vol.9, page 82.
2. J. R. Van Wazer, Phosphorus and its Compounds, Interscience, N.Y.(1958), page 972.

Constituent		Florida Land Pebble Furnace Grade		Tennessee Brown Rock Furnace Grade		Western Phosphoric Rock Low Grade	
		kg/kkg	lbs/ton	kg/kkg	lbs/ton	kg/kkg	lbs/ton
P_2O_5		2,600	5,200	2,600	5,200	2,600	5,200
CaO		3,800	7,600	3,550	7,100	3,150	6,300
MgO		35	70	75	150	190	380
Al_2O_3		125	250	1,230	2,460	810	1,620
Fe_2O_3		155	310	760	1,520	550	1,100
SiO_2		725	1,450	3,150	6,300	3,750	7,500
SO_3		215	430	50	100	260	520
F		305	610	270	540	245	490
CO_2		330	660	150	300	550	1,100
Organic Carbon		40	80	35	70	685	1,370
Na_2O		10	20	35	70	205	410
K_2O		10	20	50	100	135	270
As_2O_5	Maximum Values Quoted	0.03	0.06	0.09	0.18	0.19	0.38
BaO		-	-	0.37	0.74	1.23	2.46
B_2O_3		0.09	0.18	0.09	0.18	0.10	0.20
Cr_2O_3		0.11	0.22	0.09	0.18	1.78	3.56
CuO		0.03	0.06	0.04	0.08	0.14	0.28
MnO		0.43	0.86	3.70	7.40	0.68	1.36
MoO_3		0.04	0.08	0.01	0.02	0.34	0.68
NiO		0.04	0.08	0.01	0.02	-	-
Re_2O_3		0.60	1.20	0.25	0.50	2.46	4.92
SeO_3		0.01	0.02	0.12	0.12	0.14	0.28
TiO_2		0.60	1.20	2.50	5.00	1.37	2.74
U_3O_8		0.17	0.34	0.02	0.04	0.14	0.28
V_2O_3		0.17	0.34	0.12	0.24	5.50	11.00

If the fluoride concentration of 3.1 percent is equated to a standard raw waste load (as previously discussed) of 22 kg/kkg (44 lbs/ton), the quantities of other scrubber liquor components may be calculated:

Constituent	Raw Waste Load kg/kkg	Raw Waste Load lbs/ton
F	22	44
SiO2	8	16
P2O5	1.5	3
Fe2O3	0.5	1
S	12	24

The total CaCO3 acidity of the scrubber liquor, calculated from the above constituent quantities, is 60 kg/kkg (120 lbs/ton).

Other plants do not recirculate scrubber liquor; the volume wasted is much greater and the constituent concentrations are

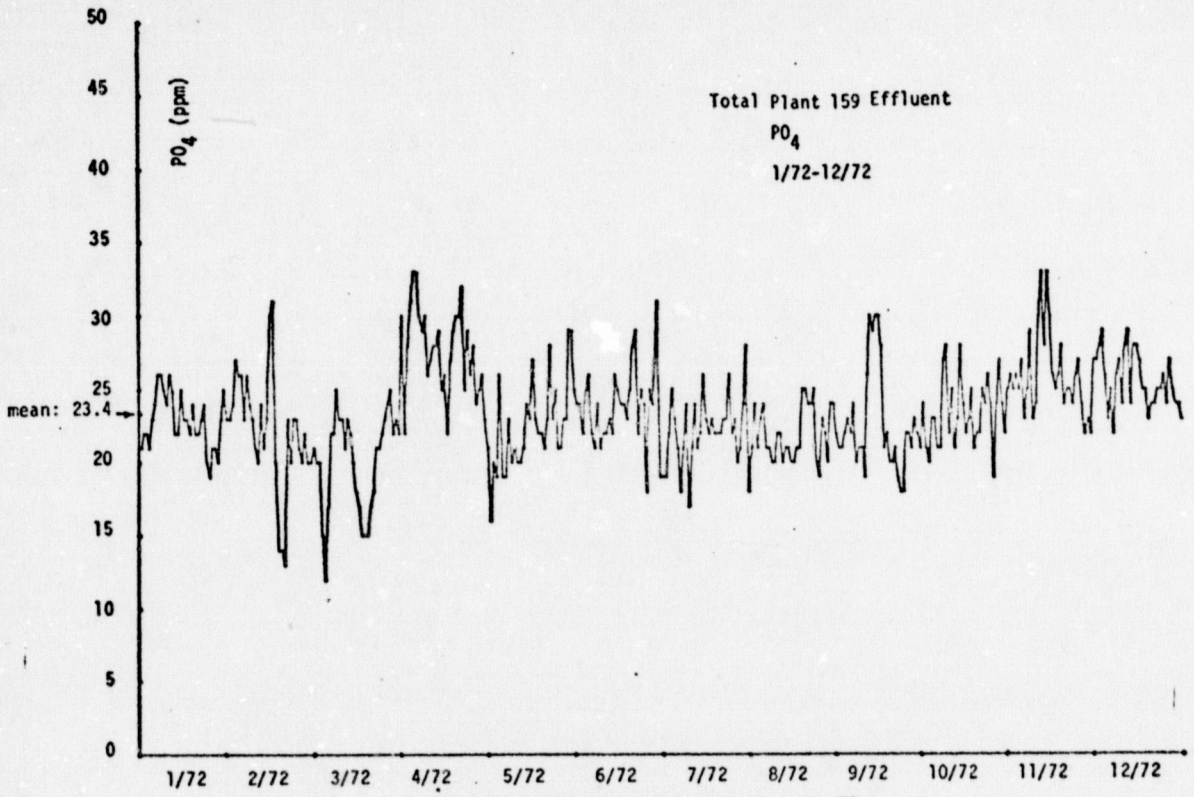

Figure 13. Phosphate Concentration vs. Time

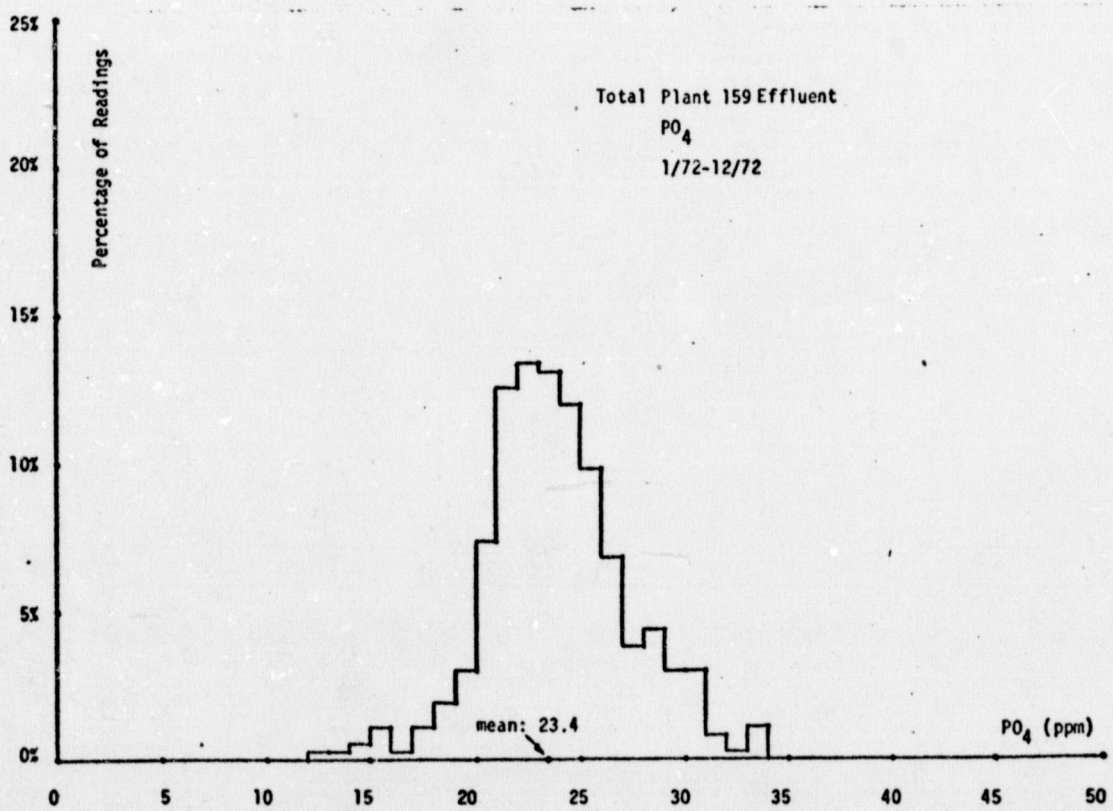

Figure 14. Histogram of Phosphate Concentration Data

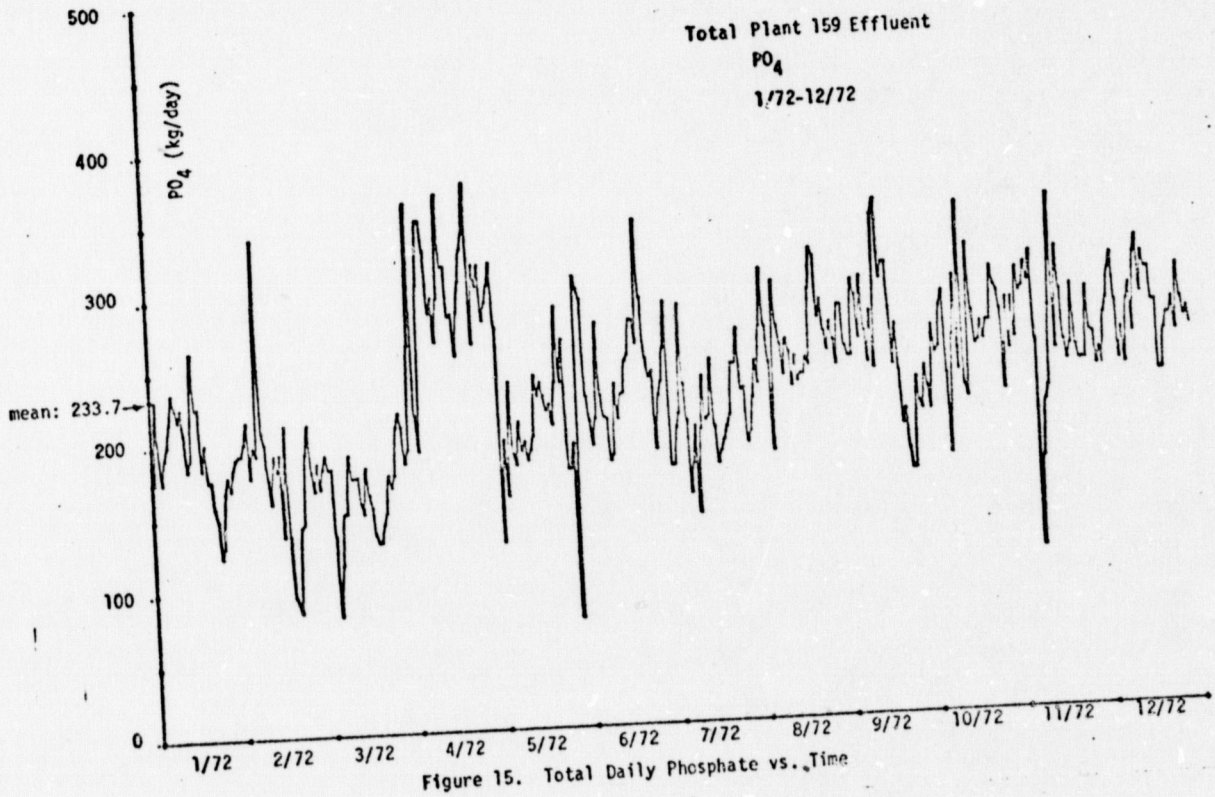

Figure 15. Total Daily Phosphate vs. Time

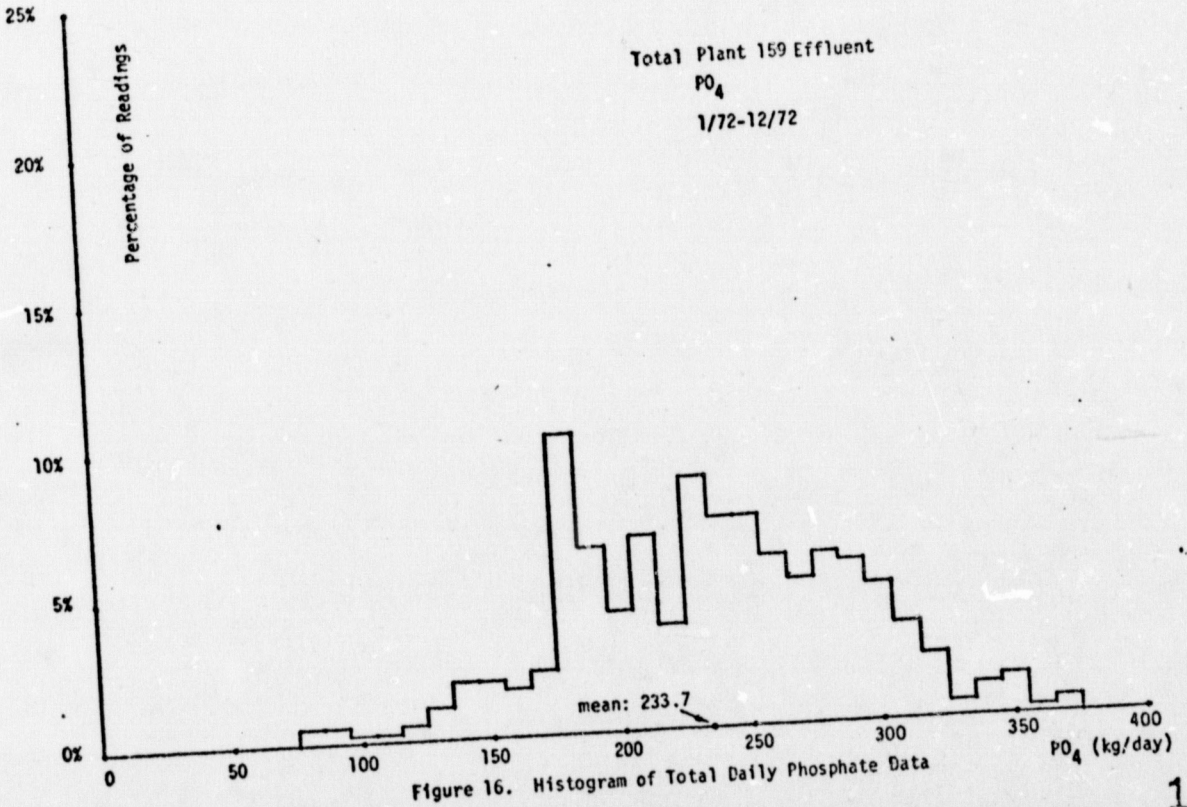

Figure 16. Histogram of Total Daily Phosphate Data

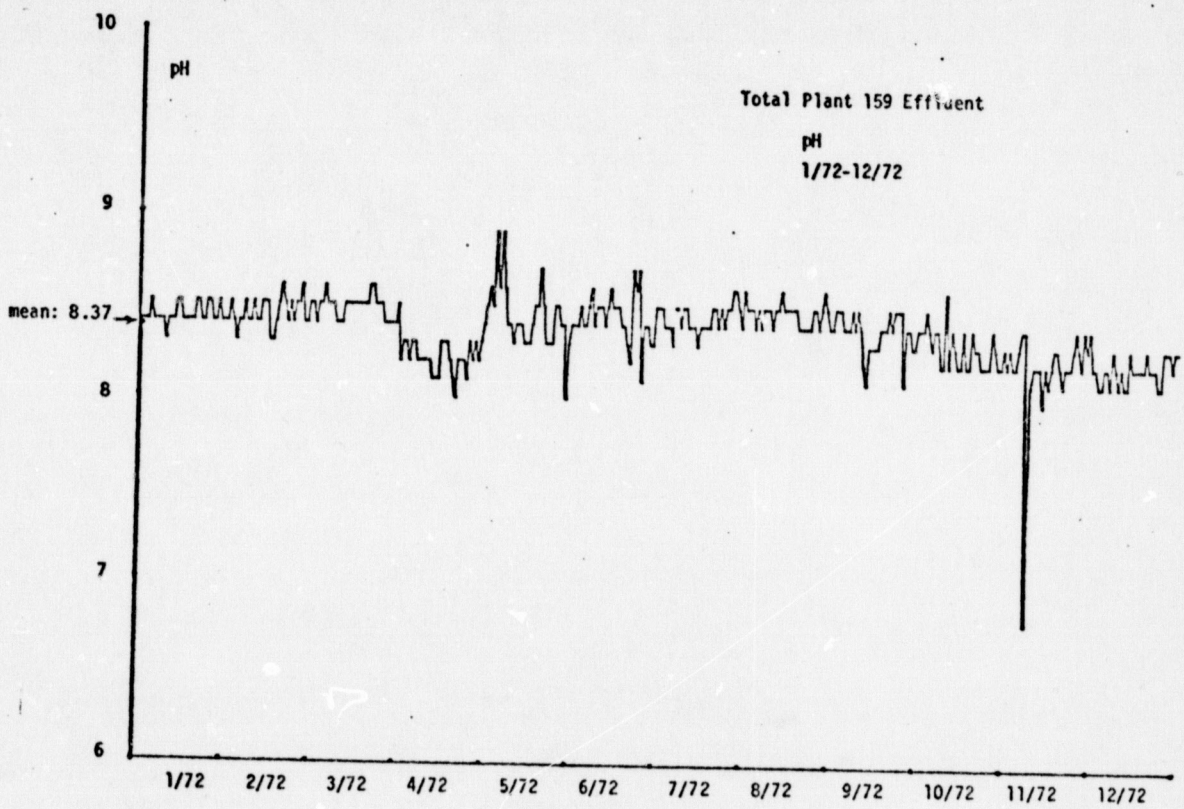

Figure 17. pH vs. Time

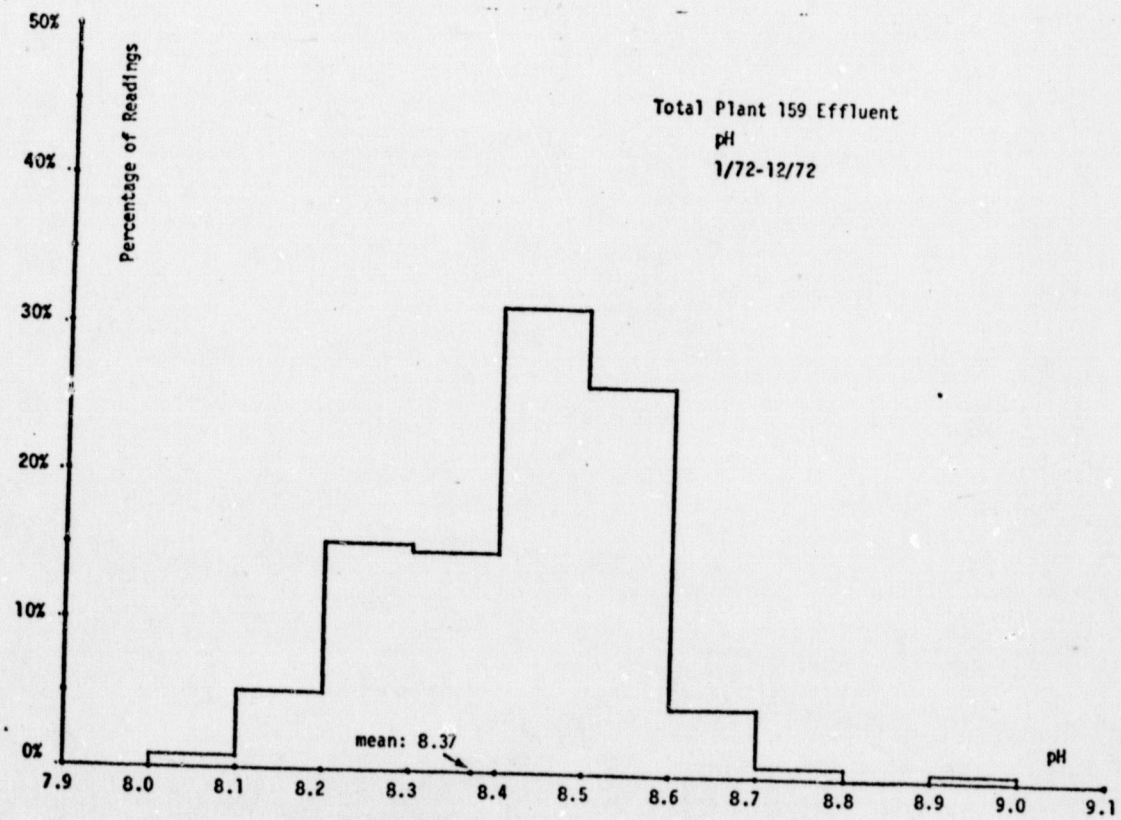

Figure 18. Histogram of pH Data

Another set of data (not sufficiently extensive to generate histograms) was obtained from Plant 037: ERRATA SHEET

Date (1973)	CaCO3 Acidity, ppm	Chloride, ppm
2/27	1170	560
2/28	1220	603
3/1	1720	822
4/19	850	447
4/23	480	305
4/24	950	532
4/25	1430	851
4/26	1250	589
4/27	1300	1035
4/30	1120	518
5/1	1470	1040
5/2	1690	716
5/3	280	773
5/4	1340	603
5/7	1810	1000
5/8	1220	574
5/9	1290	716
Mean	1217	687
Std. Deviation	384	208
95% Conf. Int. (Single Day)	±814	±441

In this case, there was no damping capacity; the acidity and chloride concentrations were closely coupled to the manufacturing process. The comparison of the 95% confidence intervals with the daily data show only one point of 17 (for acidity) and no points outside (for chloride).

Based on these very limited samples of data, it appears that the classical statistics may be applied, but with extreme caution.

For the above sets of data from Plants 159 and 037, a value of (X + 36)/ X might represent a maximum allowable daily reading as a multiple of the mean:

ERRATA SHEET

Plant	Data	$(\bar{X} + 36)/\bar{X}$
159	PO4 Concentration	1.44
	PO4 Daily Discharge	1.71
	pH	1.07
037	Acidity Concentration	1.95
	Chloride Concentration	1.91

This maximum allowable value would be extremely liberal, since a Students "t" value of 3 is equivalent to less than one reading in 100 being unduly rejected. To be even more liberal (since the data base for this analysis is extremely skimpy), the maximum value from the above table will be assumed, so that the effluent limitation guideline should be a maximum daily value no greater than twice the mean (as represented by monthly averages).

From the above discussion and data, it is apparent that pH can be controlled much more closely than other parameters. Hence, it is recommended that the daily pH limitation be the same as the corresponding monthly average limitation.

Suspended solids affect fisheries directly by covering the bottom of a stream with a blanket of material which kills out the bottom fauna, directly depriving the fish of a considerable part of their food (which lies at the bottom), or indirectly by eliminating species in the food chain. In addition, portions of the bottom, usually in the shallower parts of the stream, provide nesting sites and spawning grounds for AQUATIC LIFE .

The suspended solids directly affect fish through mechanical and abrasive action which clogs or otherwise injures the gills and respiratory structures. Although normal healthy fish secrete mucus to wash away suspended solids as they lodge on gills and other exposed parts, the synergistic action of other pollutants such as small amounts of acid wastes greatly augments the abrasion by solids by inhibiting the normal flow of mucus.(44)

Indirectly, suspended solids affect fisheries by effectively screening out the light necessary to species of flora which may be important parts of the food chain. Also indirectly, but none the less effectively, solids which settle at the bottom trap organic wastes which might otherwise be dispersed, thereby increasing the oxygen demand at the bottom of the stream with disastrous results to the bottom fauna.(44)

Of special concern in the non-fertilizer phosphorus chemicals industry is that much of the suspended solids in the raw wastes are calcium phosphates. It has recently been shown that calcium phosphates deposited in bottom muds of lakes are not inert solids, but are indeed available for uptake by the lake waters, and are a prime source of nutrients for algae blooms and a prime cause for lake eutrophication.(46)

3.0 DISSOLVED PHOSPHATES AND PHOSPHITES

Phosphites are oxidized to phosphates in streams, exerting a chemical oxygen demand upon the streams.

The controversy over the nutrient and eutrophication effects of phosphates has received much attention in recent years, resulting from the phosphate constituent in domestic wastewater. The average concentration in domestic wastewater is 30 ppm (as PO4); and the domestic waste quantities are about 1.6 kg (3.5 lbs) per capita per year, one-third of which are

from human excretions and two-thirds from synthetic detergents. (31) Runoff of synthetic fertilizers also contribute heavily to phosphate pollution of surface waters.

For the purpose of this study, it appears sufficient to rely for guidance upon the massive effort and expenditure to remove phosphates from domestic wastewater to come to the conclusion that dissolved phosphates from the industry under study are indeed a pollution parameter.

The nautural concentration of phosphates in sea water is 0.7 to 1.4 ppm.(49)

4.0 DISSOLVED SULFATES OR SULFITES

Sulfites are oxidized to sulfates in streams, exerting a chemical oxygen demand upon the streams.

Sulfates are not particularly toxic, but are a major constituent of the total dissolved solids in wastewaters from this industry (and are discussed separately as such).

5.0 DISSOLVED FLUORIDES AND FLUOROSILICATES

Fluosilicic acid and its salts are harmful materials.(48) They also decompose to form fluorides. Hydrolysis causes fluosilicates to form gelatinous precipitates which are difficult to settle and dewater in treatment operations.

Fluorides are present in natural waters in concentrations less than 1 ppm, and are widely used as drinking water additives in concentrations of a few ppm for beneficial dental effects. However, at higher concentrations than 7 or 8 ppm, fluorides have caused severe damage to bone structures. Fluorosis from airborne fluorides has been documented in cattle and in humans in the proximity of phosphate-rock mining operations, and a maximum concentration of total fluoride in air of 2.5 mg/m3 has been recommended.(48)

Fluorides and fluorosilicates are definitely harmful materials, and can be identified as pollution parameters for the purposes of this study.

6.0 DISSOLVED CHLORIDES

Dissolved chlorides are a major constituent of the total dissolved solids in wastewaters from this industry (and are discussed separately as such).

Sodium and calcium chlorides are found naturally in unpolluted waters, but are toxic to fish in high concentrations

The natural salinity of river water in the Chesapeake Estuary is 9.5 to 11.0 ppm of chloride; and the natural salinity of ocean water is 7,000 to 10,300 ppm of chloride.49)

7.0 TOTAL DISSOLVED SOLIDS

Unpolluted natural waters contain small quantities of dissolved carbonates, chlorides, phosphates, sulfates and nitrates. All of the substances in solution in river water exert osmotic pressure on the aquatic organisms, and many of these substances are physiologically active, so that the organisms have become adapted to this salt complex. Most aquatic species will tolerate changes of considerable magnitude in the relative amounts of these salts provided the total dissolved solids remains constant.(44)

The specific conductance, a direct measure of dissolved inorganic solids, lies between 150 and 500 µmhos/cm in inland streams and rivers which support good, mixed fish faunas. In the Western plains and desert areas, natural quantities of dissolved solids are higher, with specific conductance ranging to 2,000 µmhos/cm. The blood of fresh-water fish contains approximately 7,000 ppm of dissolved salts (mainly NaCl). If the total dissolved solids in the external medium exceed this 7,000 ppm by much, water will be withdrawn by osmosis from the gills of fish and from other delicate external organs of various species of aquatic life with lethal effects (as noted by the data in paragraph 6.0 for sodium chloride).(44)

8.0 ACIDITY OR LOW pH

Acidity, or low pH, kills fish through the precipitation and coagulation of the mucus on the gills and by the coagulation of the gill membranes themselves (specifically the proteins in the membranes). This precipitation and coagulation proceeds rapidly below a pH of 4.5; but species unprotected by mucus (such as Daphnia magna) are killed below a pH of 5.5

A typical State water quality standard (that of Maryland) specifies a pH of 6.0 to 8.5 regardless of water use.(50)

9.0 HEAT (HIGH TEMPERATURE)

The impact of high water temperatures takes several forms which may also act synergistically:

(a) Alteration of the physical properties of water.
(b) Decrease in the solubility of oxygen upon which most aquatic organisms depend.

(c) Increase in the rate of chemical and biochemical reactions, particularly in the oxidation of organic wastes (thereby decreasing the level of dissolved oxygen).
(d) At sufficiently high temperatures, organisms are killed directly.
(e) Physiological processes such as reproduction, development and metabolism are temperature-dependent.
(f) Temperature anomalies can block the passage of anadromous fish, greatly reducing future populations.

Most fish are poikilothermal animals whose body temperature follows changes in environmental temperatures rapidly and precisely. The tolerance of fish to high temperatures is dependent upon the normal temperature to which the fish are acclimated and to the abruptness of temperature changes (both temporally and spatially). In general, however, the upper temperature limits for fish survival are in the range of 25 to 35°C (75 to 95°F).(49,51)

A typical State water quality standard (that of Maryland) specifies the following with respect to heat rise regardless of water use(50):

Type of Water	Natural Temp,°F	Max. Temp Rise, °F	Maximum Temp,°F
Tidal	50	20	60
	50	10	90
Non-Tidal	50	20	60
	50	10	93

10.0 ELEMENTAL PHOSPHORUS

Elemental phosphorus has been identified as an extremely toxic material in very small amounts.(5) The lethal dose for humans is 100 mg and the chronic dose is 1 mg/day. Ingestion of elemental phosphorus by the human body causes bone and liver damage.

11.0 ARSENIC COMPOUNDS

The toxicity of arsenic compounds in very small amounts is well known. The Federal Water Quality Administration presented a summary of the hazards of arsenic.(47) The U.S. Public Health Service Drinking Water Standards set a maximum concentration of 0.05 ppm, with a recommended limit of 0.01 ppm.(53) There is a continuing controversy over the health hazards of minute quantities of arsenic either naturally entering the ground or surface waters; and particularly over the arsenic that occurs naturally in phosphates (at a level of As:P of 75 ppm) and is subsequently discharged into municipal wastewater.(47, 52, 53, 55, 56, 57)

12.0 VANADIUM, CADMIUM, RADIUM AND URANIUM

Phosphate rock ore may contain trace amounts of one or more of these elements. These elements are chemically and/or radioactively harmful as detailed in Reference 72.

13.0 CONCLUSION

In view of the data presented above, it is judged that all of the mentioned waste constituents generated in the non-fertilizer phosphorus chemicals industry be identified as pollution parameters as defined in the Federal Water Pollution Control Act Amendments of 1972.

2. A limited number of pollutant constituents characterizes the entire industry, crossing the lines between segments of the industry. Hence, the control and treatment techniques should be similar throughout the industry.

In this section of the report, the control and treatment technology is discussed in considerable detail. Much of this discussion is based upon observed actual abatement practice in the industry; the accomplishments of independently-verified sampling data of plant effluents.

Because the waste control and treatment challenges cross the lines between segments of the industry, the following discussion is organized according to the treatment methods and the types of raw wastes to be treated. In Section IX, Best Practicable Control Technology Currently Available, the industry is discussed on a chemical-by-chemical basis with verified effluent data presented where applicable.

2.0 IN-PROCESS CONTROLS

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices.

2.1 Segregation of Water Streams

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

Incoming pure water picks up contaminants from various uses and sources including:

1. non-contact cooling water
2. contact cooling water
3. process water
4. washings, leaks and spills

Acidity and alkalinity are detected by pH meters, often installed in-line for continuous monitoring and control.

Dissolved solids may be estimated by conductivity measurements, suspended solids and turbidity, and specific ions by wet chemistry and colorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most universal of the in-line monitoring instruments. Spills, washdowns and other contributions become quickly evident. Alarms set off by sudden pH changes alert the operators and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

Monitoring and control of harmful materials such as phosphorus and arsenic is often so critical that batch techniques may be used. Each batch can be analyzed before discharging. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. This follows from the fact that most dissolved solids are of rather low toxicity. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates, and other low ion concentrations.

3.0 TREATMENT OF SPECIFIC WASTE CONSTITUENTS

3.1 Neutralization of Acidic Wastewaters

Virtually every manufacturing process in the non-fertilizer phosphorus chemicals industry results in a raw waste load of significant acidity. In some cases, advantage is taken of the availability of alkaline waste to at least partially neutralize the acid waste streams.

At phosphorus-producing plants, some neutralization of acidic calciner scrubber liquor is achieved by the alkaline slag or by the slightly alkaline slag quench liquor (see Table 4). At TVA(7), the slag is granulated by quenching with a high-velocity jet of calciner scrubber liquor plus process cooling water; the granulated slag (with its large surface area) effectively neutralizes the acidic liquors. At plants not granulating slag, the slightly-alkaline slag quench liquors are mixed with the highly-acidic scrubber liquors for partial neutralization. This is practiced at Plants 028 and 181.

Except for this one case where granulated slag is available, lime or limestone neutralization of acid waste streams is standard practice in this industry, as observed at Plants 003, 006, 028, 159, 181, and 182. The relative chemical costs reported by Downing, Kunin and Polliot(28), listed in Table 8, show that limestone or lime are far and away more economical than other neutralizing materials. Limestone is the lower cost material (approximately $11/kkg ($10/ton)) but suffers the disadvantages of slower reaction and lower obtainable pH than with lime. Lime costs are approximately $22/kkg ($20/ton).

With the exception of hydrochloric acid from PCl3 and POCl3 manufacturing facilities, every acid waste in the phosphorus chemicls industry forms insoluble or slightly-soluble calcium salts when treated with lime:

Acid	Calcium Salt	Solubility*, ppm(27,29)
H_3PO_4	$Ca(H_2PO_4)_2.H_2O$, MCP	18,000
"	$CaHPO_4.2H_2O$, DCP	200
"	$Ca_3(PO_4)_2$, TCP	25
HF, H_2SiF_6	CaF_2	16
H_2SiO_3	$CaSiO_3$	95
H_2SO_4	$CaSO_4.2H_2O$	2,410
H_2SO_3	$CaSO_3.2H_2O$	43
H_3PO_3	2 $CaHPO_3.3H_2O$	(Slightly Soluble)

*Between 17°C and 30°C.

It is readily apparent that lime treatment (with excess lime) not only performs neutralization of acidic wastewaters from the non-fertilizer phosphorus chemicals industry, but also demineralizes most wastewaters by precipitating calcium salts. This then produces a solid waste which may be disposed of by landfilling.

3.2 Treatment of Arsenic-Rich Residues

Arsenic-rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. The common disposal method is burial in a controlled area, as practices at Plants 075, 119, 147 and 192.

The arsenic-rich liquid residue from the PCl3 distillation is more difficult to dispose of. At Plant 037, this residue is first treated with trichloroethylene, in which PCl3 is miscible but AsCl3 is not. The trichloroethylene is then water-washed

to remove the arsenic-free PCl3 and the trichloroethylene is reused. The AsCl3-rich residue is then segregated and stored in drums for final disposal.

3.3 Control and Treatment of Phossy Water at Phosphorus-Producing Plants

Because of the extreme toxicity of elemental phosphorus in small concentrations in wastewater,(5) and because complete removal of the phosphorus from the water is not practical, it is univeral practice at phosphorus-producing plants to reuse the phossy water after treatment (which is required to removed other constituents in the wastewater which would otherwise build up to concentration).

Barber(5) discusses several methods tried experimentally to remove elemental phosphorus from phossy water. Among these methods were chlorination, which was tried more than 20 years ago and which was discarded at that time because "accurate chlorinator control was found to be impractical". With the development of chlorine analyzer-controllers for municipal wastewater treatment, however, it appears that chlorination deserves another trial. Air-oxidation was attempted, but the reaction was far from complete, leaving 14 to 37 per cent of the original colloidal phosphorus unoxidized. Filtration of the colloidal phosphorus was investigated but found impractical. As a result of these discouraging results, the industry has adopted the route of containment and reuse rather than treatment and discharge.

At the TVA Muscle Shoals plant(5), a commercial flocculant, at a concentration of 40 ppm, is employed to settle both the phosphorus and the suspended solids. Using a clarifier, the system removes 92 to 93 per cent of both the phosphorus and the suspended solids as the phosphorus sludge underflow (which is only 2 per cent of the wastewater volume). The presence of suspended solids is necessary for efficient removal by this method.

The underflow from the clarifier may be treated as other phosphorus muds or sludges are treated. The sludge may be gravity-thickened and/or dewatered by centrifugation or filtration. The sludge, thickened sludge, or sludge cake (with respectively lower moisture contents) may then be heat-dried in an inert atmosphere using the process byproduct carbon monoxide as fuel. Elemental phosphorus (nominally 40 to 65 per cent of the "solids" in the sludge) are recovered. The remaining non-volatile solids contain no elemental phosphorus and can be safely disposed of or recycled to the feed preparation section of the phosphorus manufacturing plant.

Like lime treatment of phosphoric acid, lime treatment of acidic fluoride wastes is enhanced by the decreased solubility of CaF2 at high pH:

$$CaF_2(s) \quad Ca^{2+} + 2F^- \xrightarrow{2H_2O} Ca^{2+} + 2OH^- + 2HF$$

The equilibrium is driven to the far left by the addition of excess lime. The theoretical solubility of CaF2 may be calcined in much the same manner as outlined for Ca3(PO4)2, using the ionization constant of HF and the purewater solubility data for CaF2.

There has been recent commercial interest in recovering the fluoride values in acidic wastewaters. Two commercial processes have been developed to manufacture hydrofluoric acid(43), and one to manufacture synthetic cryolite for the aluminum industry.(7)

3.4.3 Treatment of Acidic Sulfite, Sulfate, and Phosphate Wastes

These acids are components of the waste streams from the phosphorus-consuming segment of the industry; and sulfuric acid is also a constituent of the wastes from the phosphorus-production segment. The sulfurous and phosphorus acids may be partially oxidized prior to treatment to sulfuric and phosphoric acids.

The neutralization and precipitation of the slightly soluble calcium salts is exactly comparable to the treatment of acidic phosphate and fluoride wastes. The solubilities of calcium sulfite and of calcium phosphite are repressed by excess lime as in the previously-discussed cases, but the solubility of calcium sulfate (a salt of a strong base and a strong acid) is not affected by pH.

3.5 Removal of Suspended Solids

The raw waste streams from the phosphorus-producing segment and from the phosphate segment of the industry contain considerable quantities of suspended solids. Moreover, the chemical treatment of acidic wastes described in the previous section produced in many instances, additional suspended solids.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids. They are in use at Plants 006, 028, 119, 159, 181 and 182. Removal of suspended solids generates a solid waste effluent which must be disposed of by landfilling.

An ion exchange may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge and an exchangeable ion carrying an opposite charge. The inert matrix is usually cross-linked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

$$RSO3H + NaCl = RSO3Na + HCl$$
$$RCO2H + NaCl = RCO2Na + HCl$$

The above reactions are reversible and can be regenerated with acid.

Anion exchangers use basic group such as the amino family.

$$RNA3OH + NaCl = RNA3Cl + NaOH$$

This is also a reversible reaction and can be regenerated with alkalies. The combination of water treatment with both cation and anion exchangers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 9 gives the level of total dissolved solids that is achieved.

Special ion exchange systems have been developed for treating high dissolved solids content(more than 1000 mg/liter total dissolved solids), minimizing regenerant chemicals costs.

3.6.2 Reverse Osmosis

The phenomenon of osmosis has its explanation in thermodynamic equilibrium and free energy concepts. Essentially, when a semipermeable membrane separates a pure liquid and solution of dissolved material in the same liquid there is a net migration of the pure liquid to the solution, driven by the free energy difference between the two sides of the membrane. Equilibrium is reached only when the liquids on each side of the membrane are of the same composition or sufficient additional pressure is applied on the solution side of the membrane to counterbalance

7. The feasibility and attractiveness of joint municipal/industrial wastewater treatment, which is a highly local evaluation to be made. Increasingly more examples of such dual treatment are being reported.(59,60,62).

8. The local solid waste management situation. The sludges from applying wastewater treatment technologies may be landfilled at highly different costs, depending upon the local availability of disposal sites and the distances involved.(63,64)

In appreciation of all of the above factors, the discussion of costs in this Section is formulated to be generally useful in evaluating the economics for any particular plant within the industry.

1.1 Current Selling Prices

Table 10 shows the current list prices of the chemicals within this industry. These data are useful as a yardstick for measuring the economic impact of achieving pollution control. Also included is a summary of estimated costs for attainment of zero discharge by representative plants.

1.2 Capital Cost Basis

The capital costs quoted in this Section have been adjusted to 1971 dollars, using the Chemical Engineering Plant Cost Index (1957-59 = 100; 1971 = 132.2). Only equipment specific to waste treatment is discussed in detail; There are sufficient sources already available for estimating standard items such as pipe, pipe fittings, tanks, pumps, mixers, etc.

2.0 IN-PROCESS CONTROLS

The cost of these controls are perhaps the most difficult to generalize, since they are almost wholly dependent upon the existing equipment configuration in any particular plant.

2.1 Segregation of Waste Streams

First, a plant must be surveyed to pinpoint the sources of both process water and non-contact cooling water. At one plant, there were a great many points where process water entered a common sewer, but there were relatively few cooling water sources.(30) It was much more economical to divert

Table 10. Summary of Costs for Attainment of Zero Discharge By Representative Plants

Chemical	Representative /Plant Capacity kkg/Day	Representative /Plant Capacity Tons/Day	Additional Capital, $	Annual Costs, $ Capital Recovery	Annual Costs, $ O&M	Annual Costs, $ Total	Annual Unit Cost $/kkg	Annual Unit Cost $/Ton	Current List Price $/kkg	Current List Price $/Ton	Cost as Pct. of List Price
Phosphorus	136	150	500,000	125,000	103,200	228,200	5.10	4.60	419	380	1.2
Phosphoric Acid (75%)	182	200	95,000	23,800	19,100	42,900	0.72	0.65	164	149	0.4
Phosphorus Pentoxide	18	20	20,000	5,000	4,100	9,100	1.55	1.40	441	400	0.4
Phosphorus Pentasulfide	36	40	49,500	12,400	10,400	22,800	1.90	1.70	299	271	0.6
Phosphorus Trichloride	36	40	20,500	5,100	13,200	18,300	1.55	1.40	292	265	0.5
Phosphorus Oxychloride	23	25	15,900	4,000	6,100	10,100	1.40	1.25	270	245	0.5
Sodium Tripolyphosphate	182	200	0	0	0	0	0	0	179	162	0
Dicalcium Phosphate (Feed Grade)	182	200	186,000	46,500	45,100	91,600	1.55	1.40	82	74	1.9
Dicalcium Phosphate (Food Grade)	182	200	33,000	8,300	88,900	97,200	1.65	1.50	286	259	0.6

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3.2 Treatment of Arsenic-Rich Residues

The cost of this solvent is rather nominal because the quantities of waste involved are only a very small fraction of the production volume, and because the solvent (trichloroethylene) is reused; despite the high unit costs which is more than 10 cents/cu m (40 cents/1,000 gal).(65) There is virtually no power requirement. There is,however, a very substantial impact upon solid waste management, since the residues are extremely toxic and must be disposed of in special ways. The quantity involved is 0.05 kg of AsCl3 per kkg of product PCl3 (0.1 lbs/ton).

3.3 Control and Treatment of Phossy Water

Control and treatment of phossy water is a universal practice at phosphorus-producing plants. Although several different methods were observed, every plant prevents the discharge of virtually all elemental phosphorus. This technology is therefore so universally applied that costs need not be estimated -- the price has already been paid. Similarly, a discussion of energy and of non-water quality aspects would be academic.

3.4 Removal of Suspended Solids

3.4.1 Settling Ponds

Using a detention time of 7 days and a depth of 3 m (10 ft), the calculated overflow rate is 0.42 cu m/day/m2 (10 gpd/ft2). This is equivalent to 4,200 cu m/day/hectare (435,600 gpd/acre).

The capital costs for small unlined ponds, with areas from 0.4 to 2 hectares (1 to 5 acres) can be estimated as(67-69):

$$\text{Capital Cost} = \$50{,}000 \times \text{Acres} - \$8{,}000 \times (\text{Acres})2$$

(Note: Hectares = 0.405 x Acres)

Because diking is a large portion of pond costs, and because the dike length increases much more slowly then pond area, larger ponds are considerably cheaper per unit area. For large unlined ponds of 40 to 1,000 hectares (100 to 2,400 acres), the capital cost is $2,500 to $12,500 per hectare ($1,000 to $5,000 per acre).(66)

For lined ponds, the additional installed capital cost for a 30-mil PVC liner is $21,500 per hectare ($8,700 per acre).(68,69)

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2.0 GUIDELINES FOR NON-CONTACT COOLING WATERS AND BLOWDOWNS

A fundamental distinction exists between process water (defined as water which comes into contact with raw materials, intermediates, products, by-products, or gaseous, airborne, or solid wastes); and non-contact cooling water and blowdowns. In the industry today, segregated cooling water is separately discharged in many cases; in other situations, cooling and process waters are mixed prior to treatment and discharge.

The recommended Level I limitations on the discharge of non-contact cooling water and blowdowns are as follows:

(a) An allowed discharge of all non-contact cooling waters provided that the following conditions are met:

(1) No harmful or hazardous pollutants are added. Cooling waters discharged must not have levels of chromate or other pollutants higher than that of the intake water or receiving water, whichever is lower.

(2) Thermal pollution be in accordance with Environmental Protection Agency Policy.

(3) All non-contact cooling waters should be monitored to detect leaks from the process and provisons should be made for emergency treatment prior to release.

(4) No untreated process waters be added to the cooling waters prior to discharge.

(b) An allowed discharge of water treatment, cooling tower and boiler blowdowns provided these do not contain harmful or otherwise hazardous materials such as chromium or cadmium, and are within the required pH range of 6 to 9 as measured both as a daily maximum and as a monthly average.

3.0 PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gaseous, airborne, or solid wastes. All values of guidelines and limitations presented below for total dissolved solids (TDS), total suspended solids (TSS), heavy metals and harmful pollutants and

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TABLE 13 - Summary of Control & Treatment Techniques at Phosphorus-Producing Plants
(For Process Waters Other Than Phossy Water)

	TSS	Total Acidity (Alkalinity)	TDS	Fluoride	Sulfate	Total Phosphate
Raw Waste Loads (from Sec. V)						
Kg/Kkg	42.5	54.5	-	53.5	111	25
lbs/ton	85	109	-	107	222	50
Waste Discharged, Kg/Kkg:						
TVA	-- No Waste Water Discharge					
Plant 181	- No Waste Water Discharge					
Plant 028 (Net)	0.5	1	4	0.1	2	0.2
Plant 159 (Gross)	0.5	(12)	22	0.04	3	0.8
Waste Discharged, lbs/ton:						
TVA	- No Waste Water Discharge					
Plant 181	- No Waste Water Discharge					
Plant 028 (Net)	1	3	9	0.2	4	0.4
Plant 159 (Gross)	1	(24)	45	0.07	7	1.6
Control & Treatment Efficiency, Per Cent:						
TVA	100	100	100	100	100	100
Plant 181	100	100	100	100	100	100
Plant 028	99	-	-	99+	98	99
Plant 159	99	-	-	99+	97	97

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In view of these different practicable alternates, the recommended Level I effluent guideline is zero discharge. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste load as estimated in Section V.

This guideline also applies to any arsenic-rich residues from the purification of P_2S_5; these solid residues may be disposed of by burial as in Plants 147 and 192.

3.2.5 Phosphorus Trichloride Manufacture

The acid wastes from phosphorus trichloride manufacture arise from the hydrolysis of PCl_3 in scrubber water from the reactor/still, from product storage tanks, from product transferring operations and from container cleaning. The scrubber water may be collected in a sump and recycled to decrease the wasted quantity of scrubber water (while still maintaining sufficient scrubber flow rates for effective mass transfer) and to increase the concentration of waste constituents.

Lime treatment of the wasted water would neutralize the acids and would precipitate the phosphite and phosphate wastes as calcium salts. Subsequent sedimentation in a mechanically-raked clarifier, with the use of a polymeric flocculant, could effectively remove 85 per cent of the suspended solids as a sludge (see Section 3.5.1). This sludge may then be hauled as a slurry for direct landfill, or may be dewatered in sand drying beds or mechanically prior to landfilling. The clarified water may then be discharged, with the following recommended Level I effluent guidelines:

Total Dissolved Solids,	5 kg/kkg (10 lbs/ton)
Total Suspended Solids,	0.7 kg/kkg (1.4 lbs/ton)
pH	6 to 10.5

The relaxation of the general pH guidelines to permit high-pH discharge in this case is to allow effective precipitation by an excess of lime. The above quantities of TSS and TDS are based upon the raw waste load as determined in Section V:

HCl	3 kg/kkg (6 lbs/ton)
$H_3PO_3 + H_3PO_4$	2.5 kg/kkg (5 lbs/ton)

The soluble $CaCl_2$ resulting from lime-neutralization of HCl is 4.5 kg/kkg (9 lbs/ton); allowing for some small amount of

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all of the resulting slurry; a practice adopted when gravity sedimentation was judged inadequate by plant personnel. Vacuum filtration (possibly after conditioning with a polymeric flocculent) can reduce the suspended solids content of the wastewater from phosphates to the level of 0.5 ppm.[30] Based upon these data and upon the level of dissolved phosphates of 0.3 ppm[31], the discharge would contain (on the basis of the total process water wasted, 4,200 l/kkg (1,000 gal/ton)):

Total Dissolved Solids,	0.0015 Kg/kkg (0.003 lb/ton
Total Suspended Solids,	0.0025 Kg/kkg (0.005 lbs/ton)

With the achievement of these extremely low levels of TDS and TSS, or even with considerable relaxation of these levels, the treated-wastewater from the manufacture of food-grade calcium phosphates then is certainly pure enough to be reused as input process water. No product purity restrictions exist any longer which had previously necessitated discharge. In fact, once the commitment towards total recycle is made, the lime treatment step may be by-passed since the ionic species from the dissolved solids and the phosphoric acid are precisely those desired in the reaction vessel.

Since the above rationale is entirely based upon demonstrated, currently-available treatment technology, the recommended Level I effluent guidelines is zero discharge.

4.0 Summary of Level I Recommended Guidelines for Process Water

4.1 Zero Discharge

The recommended Level I guidelines for process water is NO discharge OF HARMFUL POLLUTANTS for the manufacture of the following chemicals:

Phosphorus (and Ferrophosphorus)
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Sodium Tripolyphosphate
Calcium Phosphate (Food Grade)
Calcium Phosphates (Animal Feed Grade)

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4.2 Permitted Discharges

The recommended Level I guidelines for process water for the manufacture of PCl_3 and $POCl_3$ are:

	Phosphorus Trichloride	Phosphorus Oxychloride
Total Suspended Solids*:		
Kg/kkg	0.7	0.15
lbs/ton	1.4	0.3
Total Dissolved Solids*:		
Kg/kkg	5	3.5
lbs/ton	10	7
pH	6-10.5	6-10.5

The above guidelines apply to monthly average values.

Additional restrictions of these discharges would be:

1. Zero elemental phosphorus discharged.
2. Arsenic compounds permitted only at the naturally-occurring level in the discharged phosphorus compounds. Under no circumstances is the discharge of arsenic compounds permitted when they exist in an enriched state (i.e., as residues from the purification of phosphorus compounds).
3. No discharge of other metals or of HARMFUL materials is permitted.

* Suspended solids are essentially calcium phosphate and the dissolved solids are calium chloride.

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d. process changes;

e. cost of achieving the effluent reduction resulting from application of Level II technology; and

f. non-water quality environmental impact (including energy requirements).

2.0 GUIDELINES FOR NON-CONTACT COOLING WATERS AND BLOWDOWNS

The Level II guidelines are the same as for Level I except that monitoring shall be required for process leaks and provisions shall be made for emergency holding facilities for cooling water contaminated by leaks until such time as they can be treated.

3.0 PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gaseous, airborne, or solid wastes. All values of guidelines and limitations presented below for total dissolved solids (TDS), total suspended solids (TSS), metals and harmful pollutants, and other parameters are expressed as monthly averages in units of pounds of parameter per ton and kilograms of parameter per metric ton of product produced except where expressed as a concentration. Where zeros appear for a parameter when there is discharge of process wastewater, the zero means no increase above that of the intake or receiving water whichever is lower. Zero discharge of process wastewater means that no process water be discharged from the plant into surrounding waterways.

Based upon the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best available control technology economically achievable in the various categories of the non-fertilizer phosphorus chemicals industry.

3.1 All Chemicals Except Phosphorus Trichloride and Phosphorus Oxychloride

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4.3 Acidity

While moderate alkalinity may be tolerated since carbon dioxide produced in secondary treatment by the microbial oxidation of organic material will provide neutralization; free mineral acidity normally cannot be tolerated by the organisms in the secondary treatment biomass. The proteins in these organisms are precipitated and coagulated at pH 4 to 5. (44)

Another strong reason for avoiding acidic contributions to publicly-owned treatment plants is that acidic wastes would drastically promote corrosion of equipment.

It is recommended that the allowable pH range be set at 6 to 10.5.

4.4 Dissolved Inorganic Solids

Dissolved inorganic solids would pass through a secondary wastewater treatment plant without being removed. Hence, reliance upon publicly-owned treatment plants would be no treatment at all with respect to dissolved solids, and it would be equivalent to direct discharge.

It is recommended that the pretreatment standards for dissolved inorganic solids be the same as the applicable Levels I, II, or III effluent limitation guidelines.

4.5 Metals or Harmful Materials

Metals or harmful materials would at best, pass through a publicly-owned treatment plant, and at worst, adversely affect the microorganisms in secondary treatment. Elemental phosphorus (as phossy water) and enriched arsenic compounds are potential substances that may be discharged into municipal sewer systems from this industry. Special attention is brought to pretreat wastes for removal of these materials.

It is recommended that the pretreatment standards for metals or harmful materials be zero discharge.

4,6 Dissolved Phosphates

While dissolved phosphates would generally pass through secondary treatment plants with the wastewater treatment plant effluent, they would affect the sludge operations. Gravity-thickened sludge (6 to 12 per cent solids) is normally conditioned with lime, ferric chloride, or alum prior to dewatering operations, although polymeric flocculents are also widely used. The phosphates would be precipitated as the calcium, ferric, or aluminum phosphate and would thus render the conditioning step ineffective by partially or totally removing the active cation from solution.

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SECTION XII

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63. R. J. Bender, Solid Waste Disposal in Chemical Plants, Power 111, 65 (March 1967).

64. G. L. Chiagouris, Analyzing the Cost of Solid Waste Disposal, Plant Engineering 26, 82-5 (March 23, 1972).

65. G. A. Sawyer, New Trends in Wastewater Treatment and Recycle, Chem Eng, July 24, 1972, p. 120-9.

66. J. C. Sonnichsew, Jr., et. al., Cooling Ponds - A Survey of the State of the Art, Hanford Engineering Development Laboratory, Report HEDL-TME-72-101 (Sept 1972).

67. Private communications from E. I. duPont (May 3 and 16, 1973).

68. J. Kumar, Selecting and Installing Synthetic Pond Linings, Chem Eng, p. 67-8 (Feb 5, 1973).

69. P. M. Rapier, Ultimate Disposal of Brines from Municipal Wastewater Renovation, CEP Sym. Series 107, 67, 340-51.

70. Private Communication from EIMCO Division, Enviro-Tech Corp., Salt Lake City, Utah.

71. Private Communication from Dorr-Oliver Co., Stamford, Conn.

72. Sax, N. I., "Dangerous Properties of Industrial Materials", 3rd Edition, 1968.

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SUPPLEMENT A

COST INFORMATION FOR WATER-BORNE WASTES IN THE NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

PHASE I
Contract No. 68-01-1513

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5 July 1973

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INTRODUCTION

This supplement to the study report contains cost-effectiveness analyses, by product and by level of control and/or treatment, to achieve the goal of zero discharge. The approach taken was to parametrically estimate the costs for unit treatment operations and to apply these estimates to specific treatment problems. The basis for the parametric cost estimates are contained in Section VIII of the main study report.

BASIS AND LIMITATIONS OF COST-EFFECTIVENESS ANALYSES

The cost-effectiveness analyses in this supplement were developed for hypothetical plants, one for each of the chemicals manufactured in this industry. Each plant was carefully defined to be representative of the plants within the industry (these definitions and rationale are presented in the following section). The benefits in effluent reduction listed for the single representative plant are truly achievable by all plants, since the control and treatment technologies detailed in the main study report were screened for their general applicability. However, it is fully recognized that the costs for achieving these benefits may vary considerably for any specific existing plant (and particularly from the costs for the single hypothetical plant) because of the following factors:

1. The degree of freedom, which personnel of each plant must retain to choose among the alternative control and treatment technologies presented in Section VII, to choose from technologies not presented in this report, and to choose any combination or permutation of these technologies.

2. The cost tradeoffs, which are unique for each plant, between in-process controls and end-of-process treatments; with material recovery being an important parameter.

3. The real raw waste load for each plant, which may be appreciably different (in either direction) from the standard raw waste loads as presented in Section V. In particular, much greater plant-to-plant variability was observed with respect to production-normalized raw wastewater quantities than with respect to production-normalized raw quantities of polluting constituents.

4. The degree of pollution abatement already installed and practiced at a particular plant. The thrust of this program was to identify exemplary plants within each segment of the industry, rather than to survey the entire industry to analyze how much must still be accomplished by non-exemplary plants.

5. The physical characteristics of each particular plant, which vary widely in the inudstry and which significantly affect the cost of applying control and treatment technologies. Among these physical characteristics are:

*Plant age, size, and degree of automation.

*Plant layout (i.e., can in-process controls be physically installed between existing units).

*Plant distances and topography (i.e., what are the installation and operating costs of recycle technologies).

*Climatic factors (temperature and evaporation/reainfall).

*Esthetic factors (i.e., is a settling pond and evaporation pond technologies).

6. The degree to which a plant is integrated with other production departments would significantly affect the cost of applying control and treatment technologies. Can waste materials from one department be used in an adjoining department (i.e., mutual neutralization of acid and alkali wastes)? Can common treatment facilities be built (trade-off between economies of scale vs. reversing the principle of segregation of wates)? Are the wastewater sewers from adjoining departments readily separable?

7. The feasibility and attractiveness of joint municipal/industrial wastewater treatment, which is a highly local evaluation to be made. Increasingly more examples of such dual treatment are being reported.

8. The local solid waste management situation. The sludges from applying wastewater treatment technologies may be landfilled at highly different costs, depending upon the local availability of disposal sites and the distances involved.

DEFINITION OF REPRESENTATIVE PLANTS

The sizes of the representative plants were chosen so that their capacities were approximately the averages of the data presented in Table 2 (page III-7) of the main study report. Although in many cases (especially in the phosphorus-consuming segment of the industry) more than one product is made at a given location, each product was addressed separately in this supplement. Cost savings due to combined treatment facilities are a distinct probability; the effect in practice would be to achieve the benefits at costs lower than those presented in this analysis

The particular assumptions in choosing representative plants were:

1. Phosphorus Manufacture -- The representative plant has already achieved zero discharge of phossy water (as much of the industry has). It has, in addition,

achieved a level of effluent reduction commeasurate with that of plant 028 (see Tables 11 and 13, pages IX-6 and IX-9, of the main study report), but still discharges 25,000 gallons per ton of treated process water into a receiving stream. Technology "A" of Table A-1 of this supplement, therefore, represents effluent reduction, with respect to the raw waste load, already achieved by the representative plant, with no additional costs required. The effluent from technology "A" is suitable for process reuse, and technology "B" is the implementation of this recycle. For the representative plant, it was assumed that the return water system traversed 1,000 yards back to the head end of the plant and had a difference in elevation of 60 feet to make up. It was also assumed that the representative plant had no severe freezing problems.

2. Phosphoric Acid Manufacture -- The representative plant had no process water discharge (including phossy water), but had not yet performed a systematic and thorough program for minimizing, collecting, and treating minor phosphoric acid leaks and spills.

3. Manufacture of P_2O_5, P_2S_5, PCl_3, and $POCl_3$ -- The representative plants for these chemicals had not yet instituted any control or treatment of acid wastewaters, but have already achieved zero discharge of phossy water. As a conservative approach for PCl_3 and $POCl_3$ manufacture, it was assumed that solar evaporation for technology "C" in Tables A-5 and A-6 was not feasible for climatic reasons so that mechanical evaporators were necessary. It was also assumed that refrigerated condensers proved less economical than larger evaporators.

   The representative plants for P_2O_5, P_2S_5, PCl_3, and $POCl_3$ are assumed not to have sufficient land for settling ponds, so that mechanically-raked clarifiers are used.

4. Sodium Tripolyphosphate Manufacture -- The representative plant has either of two situations:
   a. Dry dust collection with return of solids to the process, plus return of wet scrubber liquors to the process, has already been installed resulting in zero discharge of process wastewaters.
   b. The above controls have not been installed, but can be economically justified on the basis of product recovery.

   For either of these two situations (which cover much of the industry), no additional costs (attributable to effluent reduction benefits) are required.

5. Feed-Grade Dicalcium Phosphate Manufacture -- For control of phosphate and lime dusts and phosphoric acid mists, the representative plant has no additional required costs (attributable to effluent reduction benefits), for the same reasons as listed above for sodium tripolyphosphate manufacture.

However, it is assumed that the representative plant uses wet-process phosphoric acid and that it performs defluorination of all acid used (in practice, a good fraction of received acid may already be defluorinated). It is further assumed that the representative plants have sufficient land area for on-site settling ponds.

6. Food-Grade Calcium Phosphate Manufacture -- The representative plant is assumed to have wet scrubbers for dust-laden vent streams. Technology "A" of Table A-9 is the replacement of wet scrubbers with baghouses, but that the cost is justified by product recovery. It is assumed that at this representative plant the elimination of wet scrubbers reduces the waste load by 50 percent.

ASSUMPTIONS IN COST ANALYSES

For these analyses, the capital investment costs have been adjusted to 1971 dollars using the Chemical Engineering Plant Cost Index (1957-59 = 100; 1971 = 132.2). The capital recovery segment of the annual costs are based upon a 5-year amortization schedule, consistent with IRS regulations concerning pollution-abatement equipment and facilities; and upon an 8 percent interest rate. The resulting annual capital recovery factor (principal and interest) is 0.25046.

"Taxes and Insurance" annual cost is estimated at 5 percent of the investment cost. "Operating and Maintenance" annual cost includes labor, supervision, lab support, etc, and is estimated at 15 percent of the investment cost, exclusive of chemicals, energy and power costs (which are calculated directly for each appropriate case). Chemical costs are included in "Operating and Maintenance", but power is listed separately. The cost of lime for neutralization has been assumed at $20 per ton, and the cost of steam for evaporation has been assumed as $0.70 per thousand pounds (or $0.70 per million Btu).

COST-EFFECTIVENESS DATA

Tables A-1 through A-9 list the cost-effectiveness data for the chemicals in this industry.

TABLE A-1: WATER EFFLUENT TREATMENT COSTS

Manufacture of Phosphorus (and Bypdt. Ferrophosphorus)
Current Selling Price $380/Ton P_4
150 Tons/Day of P_4

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	—	500,000			
Annual Costs:					
Capital Recovery: (Principal and Interest)	—	125,000			
Taxes and Insurance:	—	25,000			
Operating and Maintenance Costs (excluding energy and power costs)	—	75,000			
Energy and Power Costs	—	3,200			
Total Annual Cost	—	228,200			
Cost Per Ton	—	4.60			

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
Wastewater, Gal/Ton	102,000	25,000	0		
TSS, lbs/ton	85	1	—		
TDS, lbs/ton	—	9	—		
Acidity (Alkalinity), lbs/ton	109	3	—		
Fluoride, lbs/ton	107	0.2	—		
Sulfate, lbs/ton	222	4	—		
Total Phosphate, lbs/ton	50	0.4	—		

A- Existing Control & Treatment at Representative Plant; includes complete recycle of phossy water, evaporation of some other process water, lime treatment and sedimentation of remaining process water prior to discharge (No additional cost)

B- Piping, pumping and controls for 100 % recyle of process wastewater back to head end of plant.

Use 16" CI pipe; 1,000 yards; frictional loss = 15 ft. water.
60 ft elevation + 15 ft friction = 75 ft total head.
Power = (75 ft)(21,700 lbs/min)/33,000 ≅ 50 HP ≅ 40 KW (gross) ≅ 320,000 KWH/yr
Cost @ 0.01/KWH = $3,200

TABLE A-2: WATER EFFLUENT TREATMENT COSTS

Manufacture of Phosphoric Acid (75%)
Current Selling Price $149/Ton
200 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	95,000				
Annual Costs:					
Capital Recovery: (Principal and Interest)	23,800				
Taxes and Insurance	4,800				
Operating and Maintenance Costs (excluding energy and power costs)	14,300				
Energy and Power Costs	—				
Total Annual Cost	42,900				
Cost Per Ton	0.65				

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels
Wastewater, lbs/Ton (Phosphoric Acid Leaks & Spills)	2	0

A- Tighten Housekeeping & Maintenance; dike & dam around pumps, valves, tanks, etc; provide sumps and sump pumps; treat with lime and landfill the sludge.

TABLE A-3: WATER EFFLUENT TREATMENT COSTS

Manufacture of Phosphorus Pentoxide
Current Selling Price $400/Ton
20 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	20,000				
Annual Costs:					
Capital Recovery: (Principal and Interest)	5,000				
Taxes and Insurance	1,000				
Operating and Maintenance Costs (excluding energy and power costs)	3,000*				
Energy and Power Costs	-				
Total Annual Cost	9,000				
Cost Per Ton	1.40				

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels				
Wastewater, Gal/Ton	120	0				
$H_3PO_3 + H_3PO_4$, Lbs/ton	0.5	—				

A- Lime treatment, settling tank, recycle of tank overflow back to process; and landfilling of sludge.

* Includes $100 for Lime

TABLE A-4: WATER EFFLUENT TREATMENT COSTS

Manufacture of Phosphorus Pentasulfide
Current Selling Price $271 /Ton
40 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	12,500	37,000			
Annual Costs:					
Capital Recovery: (Principal and Interest)	3,100	9,300			
Taxes and Insurance	600	1,900			
Operating and Maintenance Costs (excluding energy and power costs)	1,900	6,000 *			
Energy and Power Costs	—	—			
Total Annual Cost	5,600	17,200			
Cost Per Ton	0.40	1.30			

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels				
Wastewater, Gal/Ton	7,200	720	0			
H_2SO_3, lbs/ton	2	2	—			
$H_3PO_3 + H_3PO_4$, lbs/ton	1	1	—			

A- Recycle scrubber water to increase constituent concentrations and decrease wastewater quantity.

B- Lime treatment, settling tank, recycle of tank overflow back to process; and land-filling of sludge.

* Includes $500 for Lime

TABLE A-5: WATER EFFLUENT TREATMENT COSTS

Manufacture of Phosphorus Trichloride
Current Selling Price $265/Ton
40 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	4,200	12,300	4,000		
Annual Costs:					
Capital Recovery: (Principal and Interest)	1,000	3,100	1,000		
Taxes and Insurance	200	600	200		
Operating and Maintenance Costs (excluding energy and power costs)	600	3,300*	600		
Energy and Power Costs	—	—	7,700		
Total Annual Cost	1,800	7,000	9,500		
Cost Per Ton	0.15	0.55	0.70		

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
Wastewater, Gal/Ton	1,200	120	100	0	
HCl, lbs/ton	6	6	—	—	
$H_3PO_3 + H_3PO_4$, lbs/ton	5	5	—	—	
TDS, lbs/ton	—	—	10	—	
TSS, lbs/ton	—	—	1.4	—	
pH	2	1.5	6-10.5	—	

A- Recycle scrubber water to increase constituent concentrations and decrease wastewater quantity.

B- Lime treatment, settling tank, landfilling of sludge.

C- Evaporation

* Includes $1,400 for Lime

TABLE 1-6: WATER EFFLUENT TREATMENT COSTS

Manufacture of Phosphorus Oxychloride
Current Selling Price $245/Ton
25 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	2,200	12,000	1,760		
Annual Costs:					
Capital Recovery: (Principal and Interest)	600	3,000	400		
Taxes and Insurance:	100	600	100		
Operating and Maintenance Costs (excluding energy and power costs)	300	2,300*	300		
Energy and Power Costs	—	—	2,400		
Total Annual Cost	1,000	5,900	3,200		
Cost Per Ton	0.15	0.70	0.40		

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels				
Wastewater, Gal/Ton	600	60	50	0		
HCl, lbs/ton	4	4	—	—		
$H_3PO_3 + H_3PO_4$, lbs/ton	1	1	—	—		
TDS, lbs/ton	—	—	7	—		
TSS, lbs/ton	—	—	0.3	—		
pH	2	1.5	6-10.5	—		

A - Recycle scrubber water to increase constituent concentrations and decrease wastewater quantity.

B - Lime treatment, settling tank, landfilling of sludge.

C - Evaporation

* Includes $500 for Lime

Manufacture of Sodium Tripolyphosphate (Tech.)
Current Selling Price $162 / Ton
200 Tons / Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	—				
Annual Costs:					
Capital Recovery: (Principal and Interest)	—				
Taxes and Insurance:	—				
Operating and Maintenance Costs (excluding energy and power costs)	—				
Energy and Power Costs	—				
Total Annual Cost	—				
Cost Per Ton	—				

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels
Wastewater, Gal/Ton	0	0

Note: In-process controls such as dry dust collection & scrubber water return to process have either been already in existence at the Representative plant, or may be economically justified on the basis of product recovery.

TABLE A-8 : WATER EFFLUENT TREATMENT COSTS

Manufacture of Dicalcium Phosphate (Feed Grade)
Current Selling Price $74 /Ton
200 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	—	186,000			
Annual Costs:					
Capital Recovery: (Principal and Interest)	—	46,500			
Taxes and Insurance	—	9,300			
Operating and Maintenance Costs (excluding energy and power costs)	—	35,800*			
Energy and Power Costs	—	—			
Total Annual Cost	—	91,600			
Cost Per Ton	—	1.40			

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels				
Wastewater, Gal/Ton	1,600	1,500	0			
TSS, lbs/ton	45	0	—			
Phosphates, lbs/ton	8	0	—			
HF, H_2SiF_6, H_2SiO_3, lbs/ton	24	24	—			

A- In-process controls for phosphate & lime dusts and for phosphoric acid mists are used; including dry dust collection and scrubber water return to process. These controls are already in existence at the Representative plant, or may be economically justified on the basis of product Recovery

B- Lime treatment, settling pond, recycle of clarified water to acid scrubbers, and landfilling of sludge.

* Includes $7,900 for Lime

TABLE A-9: WATER EFFLUENT TREATMENT COSTS

Manufacture of Dicalcium Phosphate (Food Grade)

Current Selling Price $259/Ton

200 Tons/Day

Treatment or Control Technologies Identified Below:	A	B	C	D	E
Investment	—	33,000			
Annual Costs:					
Capital Recovery: (Principal and Interest)	—	8,300			
Taxes and Insurance	—	1,700			
Operating and Maintenance Costs (excluding energy and power costs)	—	87,200*			
Energy and Power Costs	—	—			
Total Annual Cost	—	97,200			
Cost Per Ton	—	1.50			

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels				
Wastewater, Gal/Ton	1,000	500	0			
TSS, lbs/ton	200	100	—			
H_3PO_4, lbs/ton	60	30	—			

A- Replace wet scrubbers with baghouses. Costs are assumed entirely justified on the basis of product recovery

B- Lime treatment, filtration of slurry, recycle of filtrate to the process, and landfilling of filter cake.

* Includes $22,400 for Lime
19,800 for Polymeric Flocculant
40,000 for landfilling

SUPPLEMENT A

NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

CHEMICAL/PROCESS: PHOSPHOROS (Includes FERROPHOSPHOROS, which is by-product)

TOTAL U.S. PRODUCTION: 545,000 (Tons/year) (phosphorus basis)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(A) (Base)	0	90	Complete recycle of phossy water Evap. of some process water Lime treatment & sedimentation of remainder prior to discharge
(B) (Level I (Zero Discharge))	$4.60	10	100% recycle of process water

CHEMICAL/PROCESS: PHOSPHORIC ACID / DRY PROCESS TOTAL U.S. PRODUCTION: 1,810,000 (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(Base)	0	90%	Raw waste load level
(A) (Level I) (No Wastewater Discharge)	$0.65	10%	No wastewater discharge. Tighten housekeeping & maintenance Dike & dam around pumps, valves, tanks, etc. Provide sumps & sump pumps Treat with lime and landfill the sludge

CHEMICAL/PROCESS: PHOSPHORIC ACID / DRY PROCESS TOTAL U.S. PRODUCTION: 1,810,000 (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(Base)	0	90%	Raw waste load level
(A) (Level I) (No Wastewater Discharge)	$0.65	10%	No wastewater discharge. Tighten housekeeping & maintenance. Dike & dam around pumps, valves, tanks, etc. Provide sumps & sump pumps. Treat with lime and landfill the sludge

CHEMICAL/PROCESS: PHOSPHORUS PENTOXIDE TOTAL U.S. PRODUCTION: (WITHHELD) (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(Base)	0	100%	Raw waste load level.
(1) (Level I (P) Chlor. wastewater Discharge)	$10.705	0%	(No wastewater discharge; Lime treatment, settling tank overflow back to process, Landfilling of sludge.

CHEMICAL/PROCESS: PHOSPHORUS PENTASULFIDE TOTAL U.S. PRODUCTION: 59,000 (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
Raw waste load level (no treatment) (Base)	0	100%	
(A) Decreased wastewater	$0.40	0%	Reduce volume of wastewater discharge. Recycle scrubber water.
(B) Level II (No wastewater discharge)	$1.30	0%	No wastewater discharge. Lime treatment, settling tank, recycle of tank overflows back to process. Land filling of sludge.

CHEMICAL/PROCESS: PHOSPHOROUS TRICHLORIDE TOTAL U.S. PRODUCTION: 55,000 (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(Base)	0	100%	Raw waste load level.
(A) (Decreased Wastewater (Level I))	#0.15 / #0.65	0%	Decrease wastewater volume of discharge by recycle of scrubber water.
(B) (Level I)	#0.55	0%	Lime treatment, settling tank, and filling of sludge.
(C) (Level II, no wastewater discharge)	#0.70	0%	Evaporation to no wastewater discharge.

CHEMICAL/PROCESS: PHOSPHORUS OXYCHLORIDE TOTAL U.S. PRODUCTION: 31,000 (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(Base)	0	100%	Raw waste load level
(A) (Decreased wastewater)	$0.15	0%	Recycle scrubber water to decrease wastewater quantity.
(B) (Level I)	$0.70	0%	Lime treatment, settling tank, land filling of sludge.
(C) (Level II, zero discharge)	$0.40	0%	Evaporation to no wastewater discharge

CHEMICAL/PROCESS: SODIUM TRIPOLYPHOSPHATE TOTAL U.S. PRODUCTION: 1,040,000 (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(A) (Level I, no wastewater discharge)	0	100%	No wastewater discharge. In-process controls, such as dry dust collection and scrubber water return to process, are in existence or may be economically justified on the basis of product recover
(Base)	0		
(Level)	$ 0.65		

CHEMICAL/PROCESS: Dicalcium Phosphate Feed Grade TOTAL U.S. PRODUCTION: _____ (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(A) (Base)	0	50%	In-process controls for phosphate fines, lime dusts and H_3PO_4 mists. These are already in existence or are economically justified on the basis of product recovery.
(Level I) (No discharge)	$1.40	50%	Lime treatment, settling pond, recycle of process water to acid scrubbers, landfilling of sludge.

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CHEMICAL/PROCESS: Dicalcium Phosphate, Food Grade TOTAL U.S. PRODUCTION: _____ (Tons/year)

Level of Control & Treatment Technology	Incremental Annual Cost/ton of product	Percent of Industry Total Product at Level	Corresponding Effluent Limitation Level
(Base)	0	60%	Raw Waste load level
(A) (Reduced Waste Load)	0	30%	Replace wet scrubbers with baghouses. Costs are assumed entirely justified on basis of product recovery
(B) (Level I) (no wastewater discharge)	$1.50	10%	Lime treatment, filtration of slurry, recycle of filtrate to process, landfilling of filter cake. No wastewater discharge.

Supplement B

DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS OF PERFORMANCE

NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

PREPARED BY GENERAL TECHNOLOGIES CORPORATION FOR THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY UNDER CONTRACT NO. 68-01-1513

WORK SHEETS

AUG 6
~~JULY 10~~, 1973

$Ca_3(PO_4)_2$ 182

UNTREATED WELL H_2O

Plant Capacity = 500 tons/day

Parameter	Collection Date	Collection Time	Collection Depth	Site Number Date	Site Number Time	Site Number Depth
	mg/l	hr/day	ft/m	mg/l	hr/day	ft/m
TEMPERATURE	°C °F			°C °F		
COLOR (Platinum)	Apparent Units			Apparent Units		
TURBIDITY	FTU			FTU		
CONDUCTIVITY	micromhos/cms			micromhos/cms		
TOTAL DISSOLVED SOLIDS						
TOTAL DISSOLVED SOLIDS pH				8.0		
ACIDITY: TOTAL FREE						
TOTAL ALKALINITY: P						
T						
HARDNESS: TOTAL						
CALCIUM						
FREE CHLORINE						
CHLORIDE				0.285	70.3×10^{-6}	170.8×10^{-6}
FLUORIDE						
SULFATE						
PHOSPHATE (ortho)						
NITRATE (as N)						
HYDROGEN SULFIDE						
DISSOLVED OXYGEN						
SULFITE						
COD						
HEXAVALENT CHROMIUM						
METALS:						
ARSENIC						
IRON						
MERCURY (as Hg)						
LEAD						
CHROMIUM						
ALUMINUM						
VANADIUM						
TITANIUM						

Net figures
*-original data

TABLE $Ca_3(PO_4)_2$ PLANT NO. 182 WASTE & EFFLUENT DATA

STREAM Pond eff. vs. well FLOW 3270 cu m/day (0.864 MGD)

FLOW VERIFICATION — cu m/day (— MGD)

PLANT CAPACITY 500 tons/day of TCP

PARAMETER	COLLECTED DATA				MEASURED DATA			
	CONCENTRATION		Wt/Unit of PRODUCT		CONCENTRATION		Wt/Unit of PRODUCT	
	mg/l		kg/tkg	lbs/ton	mg/l		kg/tkg	lbs/ton
TEMPERATURE	°C	°F	XXXX	XXXX	°C	°F	XXXX	XXXX
COLOR (APPARENT)		APHA UNITS	XXXX	XXXX		APHA UNITS	XXXX	XXXX
TURBIDITY		FTU	XXXX	XXXX		FTU	XXXX	XXXX
CONDUCTIVITY		µmhos/cm.				µmhos/cm		
TOTAL SUS. SOLIDS								
TOTAL DISS. SOLIDS								
pH	≈4*		XXXX	XXXX	3.1*		XXXX	XXXX
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE	50*		0.30*	0.72*	802		4.75	11.55
SULFATE								
PHOSPHATE (ORTHO)								
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROME								
METALS: ARSENIC								
IRON								
MERCURY (µg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

...AND EFFLUENT DATA. SURVEY FOUND DATE 1 JUN 72 (Sampling 0864 hrs)
FLOW MEASUREMENTS ____ (Sampling ____)

(GPD 44)

Plant Capacity = 500 tons/day

PARAMETER	COLLECTED DATA CONCENTRATION		DAILY MASS		GTC MEASURED DATA CONCENTRATION		DAILY MASS	
	mg/l		#/day	#/ton	mg/l		#/day	#/ton
TEMPERATURE	°C	°F			°C	°F		
COLOR (CHROMATICITY)		APHA Units				APHA Units		
TURBIDITY		FTU				FTU		
CONDUCTIVITY		micromhos/cm				micromhos/cm		
TOTAL DISSOLVED SOLIDS								
TOTAL D.S. CALC.								
pH	~ 4				2.1			
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE	50		0.30	0.72	802		4.75	11.55
SULFATE								
PHOSPHATE (ORTH)								
NITRATE (ION)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROMIUM								
METALS:								
ARSENIC								
IRON								
MERCURY (ug/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

Gross Values

Net figures
*- original data

TABLE · $Ca_3(PO_4)_2$ PLANT NO. 182 WASTE & EFFLUENT DATA

STREAM Neutralization tank eff. vs well FLOW 3270 cu m/day (0.864 MGD)

FLOW VERIFICATION _____ cu m/day (_____ MGD)

PLANT CAPACITY 500 tons/day of TCP

PARAMETER	COLLECTED DATA: CONCENTRATION mg/l		COLLECTED DATA: Wt/Unit of PRODUCT kg/tkg	lbs/ton	MEASURED DATA: CONCENTRATION mg/l		MEASURED DATA: Wt/Unit of PRODUCT kg/tkg	lbs/ton
TEMPERATURE	°C	°F	XXXX	XXXX	°C	°F	XXXX	XXXX
COLOR (APPARENT)		APHA UNITS	XXXX	XXXX		APHA UNITS	XXXX	XXXX
TURBIDITY		FTU	XXXX	XXXX		FTU	XXXX	XXXX
CONDUCTIVITY		µmhos/cm				µmhos/cm		
TOTAL SUS.SOLIDS								
TOTAL DISS.SOLIDS								
pH			XXXX	XXXX	2.1*		XXXX	XXXX
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE					798		11.73	11.49
SULFATE								
PHOSPHATE (ORTHO)								
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROME								
METALS: ARSENIC								
IRON								
MERCURY (µg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

Neutralization tank effluent (GROSS)
Plant Capacity = 500 tons/day

PARAMETER	COLLECTED DATA mg/l	lbs/day	kg/day	ETC. MONTHLY DATA mg/l	lbs/day	kg/day	
TEMPERATURE	°C °F			°C °F			
COLOR (PLATINUM)	APHA UNITS			APHA UNITS			
TURBIDITY	FTU			FTU			
CONDUCTIVITY	Micro mhos/cm			Micro mhos/cm			
TOTAL DISSOLVED SOLIDS							
TOTAL SUSPENDED SOLIDS							
pH				2.1			
ACIDITY: TOTAL							
FREE							
TOTAL ALKALINITY							
HARDNESS: TOTAL							
CALCIUM							
FREE CHLORINE							
CHLORIDE							
FLUORIDE				798	4.73	11.49	Gross Value
SULFATE							
PHOSPHATE (TOTAL)							
NITRATE (AS N)							
HYDROGEN SULFIDE							
DISSOLVED OXYGEN							
SULFITE							
COD							
HEXAVALENT CHROMIUM							
METALS:							
ARSENIC							
IRON							
MERCURY (AS Hg)							
LEAD							
CHROMIUM							
ALUMINUM							
VANADIUM							
TITANIUM							

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Net figures
* - original data

TABLE . $Ca_3(PO_4)$ PLANT NO. 182 WASTE & EFFLUENT DATA

STREAM Acid Scrubber effluent FLOW 3270 cu m/day (0.864 MGD)

FLOW VERIFICATION ——— cu m/day (— MGD)

PLANT CAPACITY 500 tons/day of TCP

PARAMETER	COLLECTED DATA				MEASURED DATA			
	CONCENTRATION		Wt/Unit of PRODUCT		CONCENTRATION		Wt/Unit of PRODUCT	
	mg/l		kg/kkg	lbs/ton	mg/l		kg/kkg	lbs/ton
TEMPERATURE	°C	°F	XXXX	XXXX	°C	°F	XXXX	XXXX
COLOR (APPARENT)		APHA UNITS	XXXX	XXXX		APHA UNITS	XXXX	XXXX
TURBIDITY		FTU	XXXX	XXXX		FTU	XXXX	XXXX
CONDUCTIVITY		µmhos/cm.				µmhos/cm		
TOTAL SUS.SOLIDS								
TOTAL DISS.SOLIDS								
pH			XXXX	XXXX	1.2*		XXXX	XXXX
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY:								
P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE	2000* max		11.85*	28.30*	-1270		+7.51	+19.26
SULFATE								
PHOSPHATE (ORTHO)								
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROME								
METALS: ARSENIC								
IRON								
MERCURY (µg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

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ACID SCRUBBER
Effluent
(GROSS)

Plant Capacity = 500 tons/day

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PARAMETER	COLLECTED EARTH			ETC RETURNED EARTH		
	mg/l	kg/day	kg/ton	mg/l	kg/day	kg/ton
TEMPERATURE	°C	°F		°C	°F	
COLOUR (ABSORBANCY)		APHA UNITS			APHA UNITS	
TURBIDITY		FTU			FTU	
CONDUCTIVITY		micromhos/cm			micromhos/cm	
TOTAL DISSOLVED SOLIDS						
TOTAL SUSPENDED SOLIDS						
pH				1.8		
ACIDITY: TOTAL						
FREE						
TOTAL ALKALINITY: P						
T						
HARDNESS: TOTAL						
CALCIUM						
FREE CHLORINE						
CHLORIDE						
FLUORIDE	2000	max	11.85	28.80	732	4.34	10.54
SULFATE						
PHOSPHATE (TOTAL)						
NITRATE (as N)						
HYDROGEN SULFIDE						
DISSOLVED OXYGEN						
SULFITE						
COD						
HEXAVALENT CHROMIUM						
METALS:						
ARSENIC						
IRON						
MERCURY (ug/l)						
LEAD						
CADMIUM						
ALUMINUM						
VANADIUM						
TITANIUM						

Gross Values (approx equal to Net)

Net

*-original data

TABLE Ca$_3$(PO$_4$)$_2$ PLANT NO. 182 WASTE & EFFLUENT DATA

STREAM Cooling tower blowdown vs. well water FLOW 81.7 cu m/day (0.0216 MGD)

FLOW VERIFICATION ——— cu m/day (——— MGD)

PLANT CAPACITY 500 tons/day of TCP

	COLLECTED DATA				MEASURED DATA			
	CONCENTRATION		Wt/Unit of PRODUCT		CONCENTRATION		Wt/Unit of PRODUCT	
PARAMETER	mg/l		kg/kkg	lbs/ton	mg/l		kg/kkg	lbs/ton
TEMPERATURE	°C	°F	XXXXX	XXXXX	°C	°F	XXXXX	XXXXX
COLOR (APPARENT)		APHA UNITS	XXXXX	XXXXX		APHA UNITS	XXXXX	XXXXX
TURBIDITY		FTU	XXXXX	XXXXX		FTU	XXXXX	XXXXX
CONDUCTIVITY		µmhos/cm.				µmhos/cm		
TOTAL SUS.SOLIDS								
TOTAL DISS.SOLIDS								
pH			XXXXX	XXXXX	8.6 *		XXXXX	XXXXX
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE					.70		8.0×10^{-3}	1.6×10^{-2}
FLUORIDE								
SULFATE								
PHOSPHATE (ORTHO)								
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROMIUM								
METALS: ARSENIC								
IRON								
MERCURY (µg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

TABLE — . Log Book RUN NO. LL2 WASTE AND EFFLUENT DATA STREAM Cooling Tower Blowdown FLOW 1.2 GPM (0.0216 MGD)
FLOW VERIFICATION ——— GPM/H_2O (———)

Plant Capacity = 500 tons/day

PARAMETER	COLLECTED DATA CONCENTRATION mg/l	COLLECTED DATA MASS FLOW lbs/day	COLLECTED DATA MASS FLOW lbs/ton	ETC MEASURED DATA CONCENTRATION mg/l	ETC MEASURED DATA MASS FLOW lbs/day	ETC MEASURED DATA MASS FLOW lbs/ton
TEMPERATURE	°C °F			°C °F		
COLOR (PLATINUM)	APHA UNITS			APHA UNITS		
TURBIDITY	FTU			FTU		
CONDUCTIVITY	μmhos/cm			μmhos/cm		
TOTAL SUS. SOLIDS						
TOTAL DISS. SOLIDS				8.6		
P.I.T.						
ACIDITY: TOTAL						
FREE						
TOTAL ALKALINITY: P						
T						
HARDNESS: TOTAL						
CALCIUM						
FREE CHLORINE						
CHLORIDE						
FLUORIDE				0.99	0.00015	0.00036
SULFATE						
PHOSPHATE (AS PO4)				18	0.0027	0.0065
NITRATE (AS N)						
HYDROGEN SULFIDE						
DISSOLVED OXYGEN						
SULFITE						
COD						
HEXAVALENT CHROMIUM						
METALS:						
ARSENIC						
IRON						
MERCURY (μg/l)						
LEAD						
CHROMIUM						
ALUMINUM						
VANADIUM						
TITANIUM						

Gross Values

TABLE · $Ca_3(PO_4)_2$ PLANT NO. 182 WASTE & EFFLUENT DATA

STREAM Scrubber bleed to Process us well. (NET) FLOW 81.7 cu m/day (0.0216 MGD)

FLOW VERIFICATION ——— cu m/day (— MGD)

PLANT CAPACITY 500 tons/day of TCP

PARAMETER	COLLECTED DATA				MEASURED DATA			
	CONCENTRATION		Wt/Unit of PRODUCT		CONCENTRATION		Wt/Unit of PRODUCT	
	mg/l		kg/kkg	lbs/ton	mg/l		kg/kkg	lbs/ton
TEMPERATURE	°C	°F	XXXXX	XXXXX	°C	°F	XXXXX	XXXXX
COLOR (APPARENT)		APHA UNITS	XXXXX	XXXXX		APHA UNITS	XXXXX	XXXXX
TURBIDITY		FTU	XXXXX	XXXXX		FTU	XXXXX	XXXXX
CONDUCTIVITY		µmhos/cm.				µmhos/cm		
TOTAL SUS.SOLIDS								
TOTAL DISS.SOLIDS								
pH			XXXXX	XXXXX	4.0*		XXXXX	XXXXX
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE					15.7	.0023	.0056	
SULFATE								
PHOSPHATE (ORTHO)								
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROME								
METALS: ARSENIC								
IRON								
MERCURY (µg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

BLEED TO PROCESS (GROSS) Plant Capacity = 500 tons/day

PARAMETER	COLLECTED DATA			ETC MEASURED DATA		
	mg/l	lbs/day	kg/day	mg/l	lbs/day	kg/day
TEMPERATURE	°C °F			°C °F		
COLOR (APPARENT)	ALPHA UNITS			ALPHA UNITS		
TURBIDITY	FTU			FTU		
CONDUCTIVITY	μmhos/cm			μmhos/cm		
TOTAL SUSP. SOLIDS						
TOTAL DISS. SOLIDS						
pH				4.0		
ACIDITY: TOTAL						
FREE						
TOTAL ALKALINITY: P						
T						
HARDNESS: TOTAL						
CALCIUM						
FREE CHLORINE						
CHLORIDE						
FLUORIDE				16.0	0.0024	0.0058
SULFATE						
PHOSPHATE (as P)				6800	1.01	2.45
NITRATE (as N)						
HYDROGEN SULFIDE						
DISSOLVED OXYGEN						
SULFITE						
COD						
HEXAVALENT CHROMIUM						
METALS:						
ARSENIC						
IRON						
MERCURY (ng/l)						
LEAD						
CADMIUM						
ALUMINUM						
VANADIUM						
TITANIUM						

Gross Values

Not figures
* - original data (effluent)

TABLE · $Ca_3(PO_4)_2$ PLANT NO. 182 WASTE & EFFLUENT DATA

STREAM Dryer Scrubber 1514 cu m/day (0.4 MGD)

Recirculation Stream vs. well water FLOW VERIFICATION _____ cu m/day (_____ MGD)

PLANT CAPACITY 500 tons/day of TCP

PARAMETER	COLLECTED DATA: CONCENTRATION mg/l		Wt/Unit of PRODUCT kg/kkg	lbs/tn	MEASURED DATA: CONCENTRATION mg/l		Wt/Unit of PRODUCT kg/kkg	lbs/tn
TEMPERATURE	°C	°F	XXXX	XXXX	°C	°F	XXXX	XXXX
COLOR (APPARENT)		APHA UNITS	XXXX	XXXX		APHA UNITS	XXXX	XXXX
TURBIDITY		FTU	XXXX	XXXX		FTU	XXXX	XXXX
CONDUCTIVITY		µmhos/cm.				µmhos/cm		
TOTAL SUS.SOLIDS								
TOTAL DISS.SOLIDS								
pH			XXXX	XXXX	4.0*		XXXX	XXXX
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE					32.0	0.06	0.12	
SULFATE								
PHOSPHATE (ORTHO)								
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROME								
METALS: ARSENIC								
IRON								
MERCURY (µg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

WASTE AND EFFLUENT DATA — SYSTEM: DRYER — FLOW 514 gpm (2'04 I.D.)

SCRUBBER RECIRCULATION STREAM (GROSS)

~~Plant Capacity~~ = 500 tons/day

PARAMETER	COLLECTED DATA CONCENTRATION mg/l		COLLECTED DATA MASS FLOW lbs/day	lbs/ton	ETC MEASURED DATA CONCENTRATION mg/l		ETC MEASURED DATA MASS FLOW mg/l	lbs/ton
	°C	°F			°C	°F		
TEMPERATURE								
COLOR (UNSPECIFIED)		ALPHA UNITS				ALPHA UNITS		
TURBIDITY		FTU				FTU		
CONDUCTIVITY		micromhos/cm				micromhos/cm		
TOTAL SUSPENDED SOLIDS								
TOTAL DISSOLVED SOLIDS								
pH					4.0			
ACIDITY: TOTAL								
FREE								
TOTAL ALKALINITY: P								
T								
HARDNESS: TOTAL								
CALCIUM								
FREE CHLORINE								
CHLORIDE								
FLUORIDE					32.3		0.089	0.22
SULFATE								
PHOSPHATE (ORTHO)					4700		12.90	31.34
NITRATE (as N)								
HYDROGEN SULFIDE								
DISSOLVED OXYGEN								
SULFITE								
COD								
HEXAVALENT CHROMIUM								
METALS:								
ARSENIC								
IRON								
MERCURY (mg/l)								
LEAD								
CHROMIUM								
ALUMINUM								
VANADIUM								
TITANIUM								

Gross Values

$Ca_3(PO_4)_2$

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Overflow flow was 283.9 0.075 MGD

(TREATED WASTE WATER)

Plant Capacity = 215 tons/day

60% Di Calcium P

All values are Gross Values

PARAMETER	COLLECTION DEPTH			CONCENTRATION		
	mg/l	lbs/day	tons/day	mg/l	lbs/day	tons/day
TEMPERATURE	°C	°F		36 = 97	°F	
COLOR (APPARENT)		APHA UNITS		>500	APHA UNITS	
TURBIDITY		FTU		550	FTU	
RADIOACTIVITY		Micro c/l		7800	Micro c/l	
TOTAL SUSP. SOLIDS				1300	1.56	3.78
TOTAL DISS. SOLIDS				7160	8.57	20.82
pH				9.9		
ALKALINITY: TOTAL						
FREE						
TOTAL PHOSPHATE AS P				400	0.478	1.16
ORTHO				2900	3.47	8.43
HARDNESS: TOTAL				6	0.0072	0.017
CALCIUM				0	0	0
FREE CHLORINE						
CHLORIDE				5	0.0060	0.014
FLUORIDE					0	0
SULFATE				0	0	0
NITROGEN (AMMONIA)				3400	4.07	9.88
NITRATE (as N)				2.7	0.0032	0.0078
HYDROGEN SULFIDE						
DISSOLVED OXYGEN						
SULFITE						
COD						
CHLORINE DEMAND						
PHOSPHATES	(TOTAL INORGANIC mg/l PO_4)			21,000	25.13	61.06
METALS:						
ARSENIC						
IRON				0	0	0
MERCURY (mg/l)						
LEAD						
CHROMIUM						
ALUMINUM						
VANADIUM						
TITANIUM						

Effluent 107.0 0.02 mgd

Phosphate Flow Monitoring

Dryer Stack Wash

Plant Capacity = 215 tons/day

60% Di Calcium

All values are (grab) values

Parameter	Collected Grab Concentration mg/l	Collected Grab Mass lbs/day	Collected Grab Mass kg/day	Discharged Grab Concentration mg/l	Discharged Grab Mass lbs/day	Discharged Grab Mass kg/day
Temperature	°C / °F			°C / °F		
Color (Platinum)				>500 APHA units		
Turbidity				290 FTU		
Conductivity				340 micromhos		
Total Suspended Solids				368	0.17	0.41
Total Dissolved Solids				187	0.86	0.21
pH				8.1		
Acidity: Total				0	0	0
Free				0	0	0
Alkalinity: P				0	0	0
T				100	0.046	0.11
Hardness: Total				100	0.046	0.11
Calcium				40	0.018	0.045
Free Chlorine						
Chloride				25	0.012	0.028
Fluoride						
Sulfate				110	0.051	0.12
Phosphate (ortho)				1.65	0.00076	0.0018
Nitrate (as N)				1.7	0.00079	0.0019
Hydrogen Sulfide						
Dissolved Oxygen						
Sulfite						
COD						
Halogenated Hydrocarbons						
Phosphate (Total Inorganic) mg/l P				3.8	0.0018	0.0043
Metals:						
Arsenic				0	0	0
Iron						
Mercury (ug/l)						
Lead						
Cadmium						
Aluminum						
Vanadium						
Titanium						

Plant 003

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GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: 23 May 73

To : 303 Distribution

Re: 303-119

From : D. H. Sargent DS

Subject: Plant Visit, P_2O_5, P_2S_5, PCl_3, $POCl_3$
Hooker, Niagara Falls, N. Y. 5/10/73

Elemental phospharous, a raw material for the manufacture of P_2O_5, P_2S_5, and PCl_3, is transported to Niagara Falls under a blanket of water and is stored at the plant under water. Phossy water is displaced and wasted whenever liquid phosphorus is transferred from railroad cars to the plant storage tanks. Efforts over recent years have minimized the quantities of wasted phossy water.

These four phosphorus chemicals are readily hydrolyzed, leading to two important characteristics of their manufacture:

(1) Process water is never used; conversely, steps are taken to prevent moisture from contaminating the system.

(2) Water is always used to rapidly destroy most wastes (gaseous vents, dusts, vessel cleanouts, residues).

Hence, the aqueous raw wastes other than phossy water arise indirectly from efforts to minimize discharges to the atmosphere, from efforts to destroy hazardous solid wastes, or from plant housekeeping activities.

The specific sources of aqueous wastes include:

(1) Phossy water from transfer of liquid phosphorus.
(2) Water seals on batch reactor vent lines.
(3) Water scrubbers or water seals on continuous process vent lines.
(4) Water scrubbers for fumes from product casting, product transferring operations, and product holding tanks.
(5) Periodic cleanout of residues in semi-batch reaction vessels and still pots.
(6) Washing of returned shipping containers prior to reuse.

ANALYSIS FORM

Plant HOOKER CHEM CO. Date 22 MAY 73 Identifying No. _____

Location NIAGARA FALLS, N.Y. Sample Site P2S5

Product PHOSPHOROUS COMPOUNDS 20 TONS/DAY

Parameter	Number of Measurements	Individual Measurements	Average
Flow	GPD	82,000 *	
Temperature	°C	20	
Color (APPARENT)	APHA UNITS	80	
Turbidity	FTU	30	
Conductivity		120 mg/l NaCl; 240 micromhos/cm	
Suspended Solids	mg/l	<10	
pH		7.15	
Acidity: Total	mg/l $CaCO_3$	15	
Free	0	0	
Alkalinity (Total) P / T		0 / 35	
Hardness: Total		140	
Calcium	↓	95	
Halogens: Chlorine	mg/l Cl_2	0	
Chloride	mg/l Cl^-	45	
Fluoride	mg/l F^-	2.7	
Sulfate	mg/l SO_4^{-2}	6.4	
Phosphates (Total)	mg/l PO_4^{-3}	28	
Nitrogen (Total)	mg/l N	0.27	
Heavy Metals: Iron	mg/l Fe	4.4	
Chromate	mg/l Cr^{+6}	0	
Hydrogen Sulfide			
Oxygen (Dissolved)	mg/l O_2	8.2	
BOD			
COD	mg/l	75	

REMARKS: DYE METHOD BETWEEN TWO MANHOLES

0.6 # P4 / TON P2S5

SIGNATURE(S) Harry M Bramley

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: 19 Mar 73

To : 303 Distribution

Re: 303-59

From : C. L. Parker

Subject: Plant Visit - Hooker Chemical Co.
Jeffersonville, Ind. 3/15/73

The Jeffersonville, Ind. plant of Hooker Industrical Chemicals Division, was visited on March 15 to collect data on waste effluent and treatment practices for sodium tripolyphosphate production.

Discussions were with L. P. (Larry) Hallahan, Works Manager, T. A. (Tom) Dumstorf, Plant Engineer and Dave Ehlers.

The Jeffersonville plant makes phosphoric acid and a variety of sodium and potassium phosphates of which approximately 60 percent is STPP.

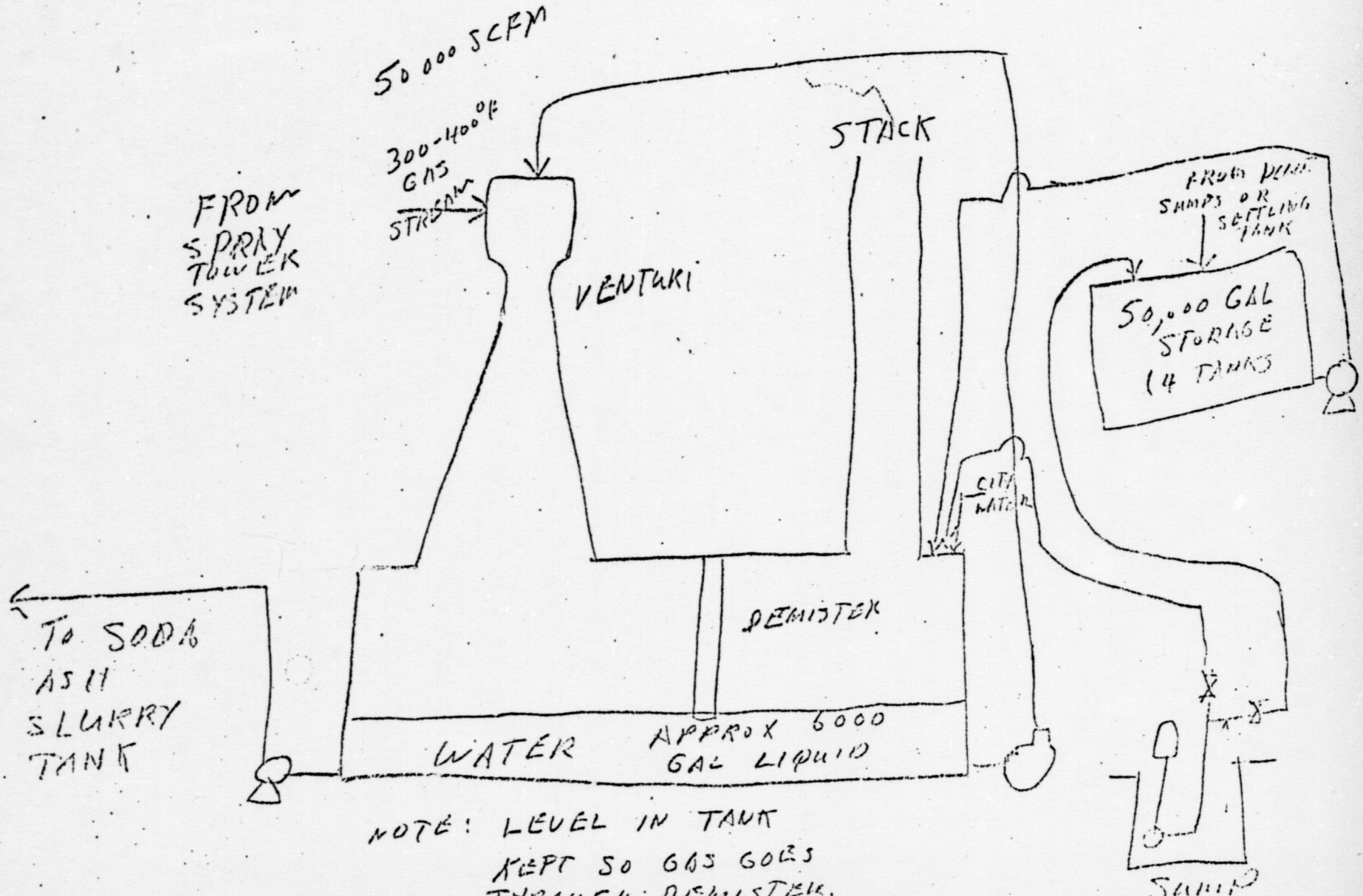
This plant, with the exception of sanitary, boiler and tower blowdowns, and water softener regeneration waste is entirely cyclized. The only stream leaving the plant is made up of the exceptions mentioned above. This stream goes to the Municipal Sewer with no problem. The collection, treatment and recycle system is exemplary. They have realized $30,000/yr savings by material recovery.

Details of the operation including process prints and historical progress measurements have been given to Ed Rissmann for his coordination.

Sampling has been arranged.

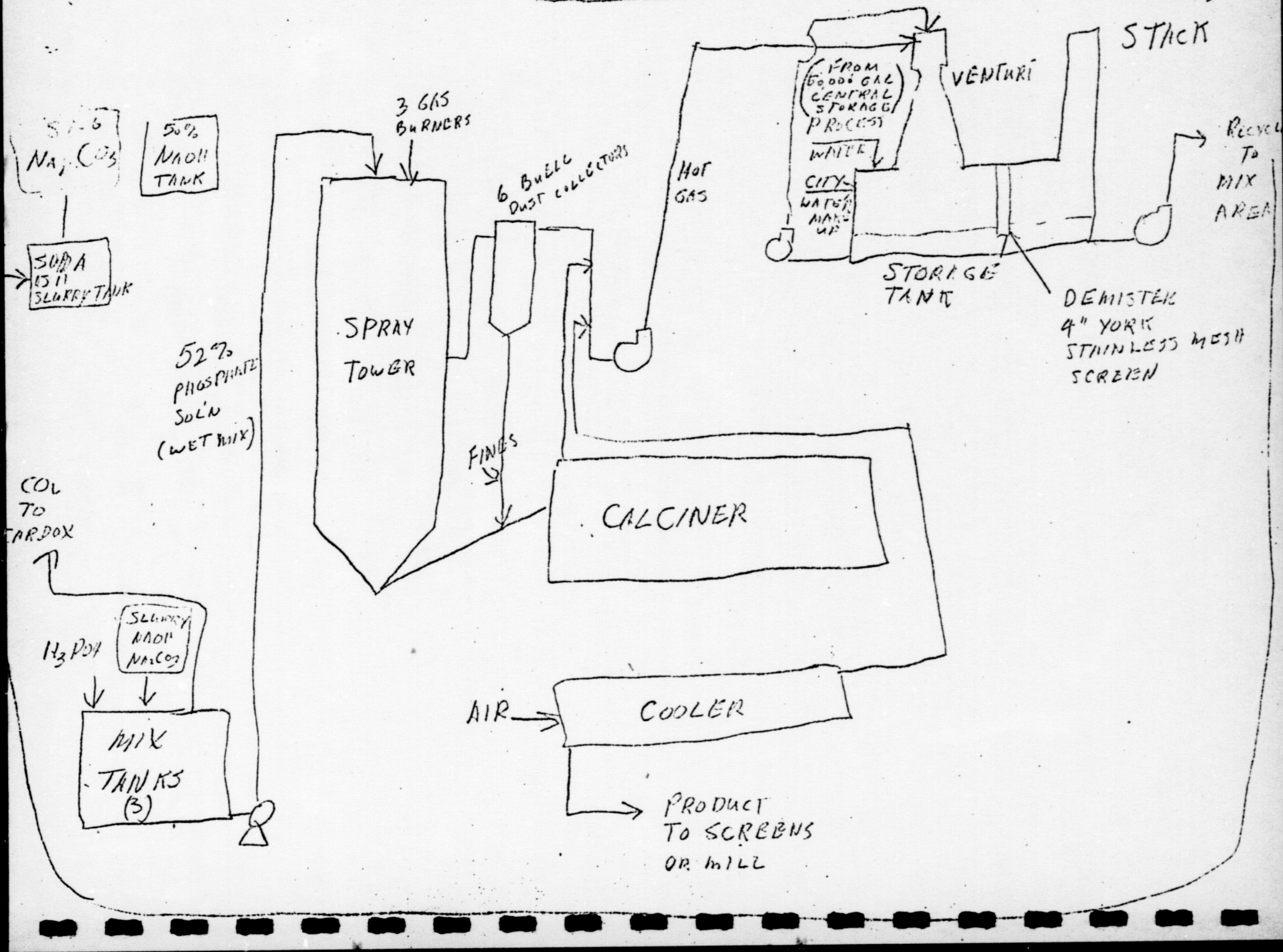
Type 3 SCRUBBER SYSTEM

SODIUM TRIPOLYPHOSPHATE FACILITY



NOTE: LEVEL IN TANK KEPT SO GAS GOES THROUGH DEMISTER. CITY WATER USED AS MAKEUP (FLOAT CONTROLLED)

STPP PROCESS



WATER INPUTS TO PLANT

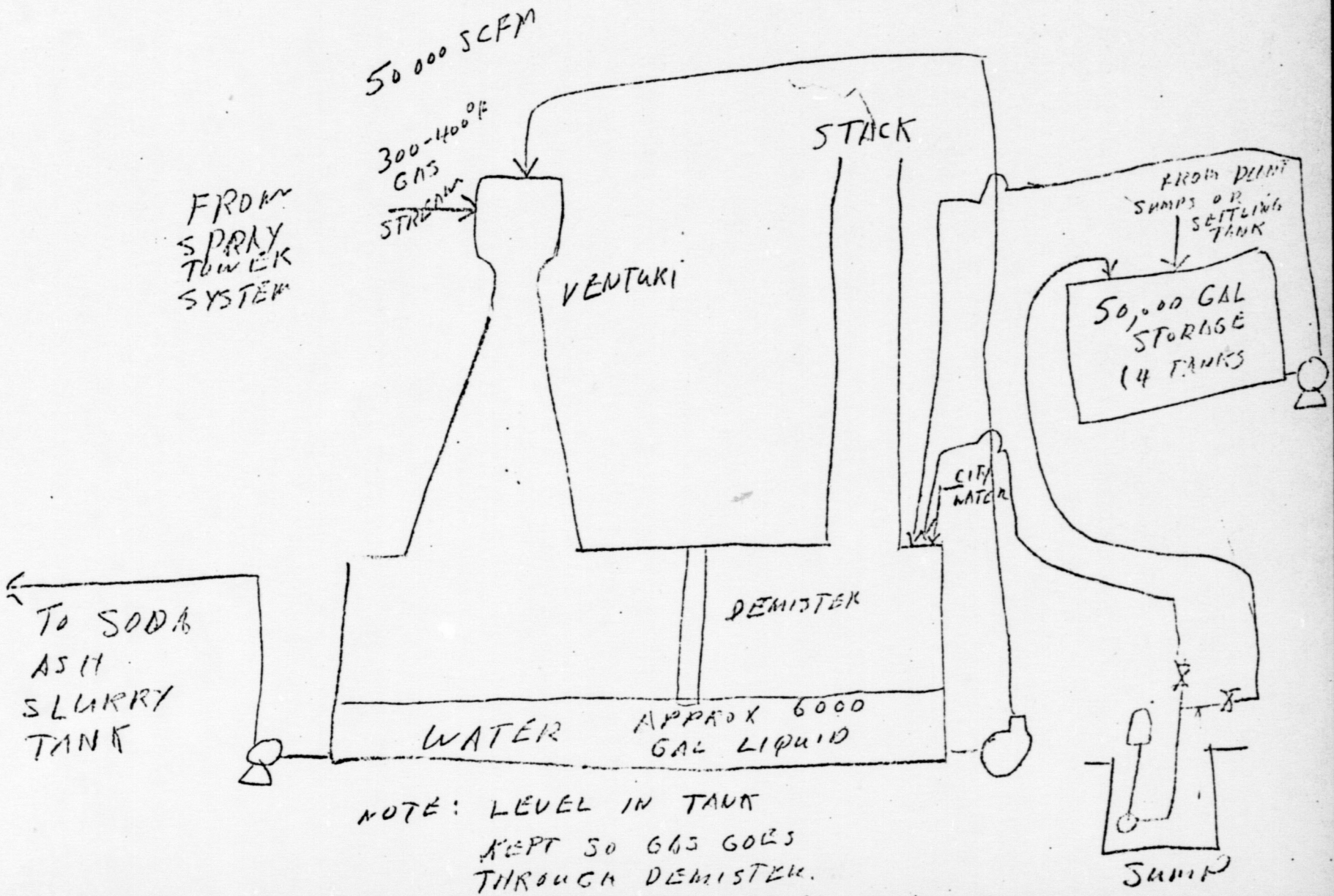
TYPE	QUANTITY, GPD	COMMENTS ON SOLIDS, MINERALS, TREATMENTS, ETC.
RIVER		
LAKE		
MUNICIPAL	— 36,000	SEE ATTACHED ANALSIS SHEETS.
WELL		
OTHER	— 14,000	(RECYCLE FROM OTHER AREAS) FILTER BACK WASH, BLEED OFF FROM COOLING TOWERS

WATER USAGE

TYPE	TOTAL QUANTITY, GPD	% RECYCLED
COOLING	5000	ALMOST 100%
PROCESS	— — — 50,000	OUT THE STACK DURING DRYING
OTHER		
OTHER		

COMMENTS

SCRUBBER



NOTE: LEVEL IN TANK
KEPT SO GAS GOES
THROUGH DEMISTER.
CITY WATER USED AS
MAKEUP [illegible]

HOOKER CHEMICAL CORPORATION — MONTH: NOVEMBER 1965
JEFFERSONVILLE, INDIANA

DATE	Flow mgd	pH	Suspended Solids mg/l	Suspended Solids lbs.	PO_4 Total Phosphate mg/l	PO_4 Total Phosphate lbs.
1	16,000	6.4	.00	0	1500	716
2	16,000	6.4	15	10	720	480
3	16,000	6.0	30	24	240	192
4	16,000	6.4	20	15	630	420
5	16,000	6.6	10	8	540	372
6	16,000	7.2	10	8	360	240
7	16,000	6.7	20	8	710	237
8	16,000	6.4	10	4	310	124
9	16,000	6.6	.00	0	470	236
10	16,000	6.9	10	8	260	110
11	16,000	7.0	.00	0	710	372
12	16,000	7.1	10	8	510	510
13	16,000	7.1	.00	0	1500	716
14	16,000	7.0	10	8	1500	716
15	16,000	7.2	.00	0	1200	672
16	16,000	7.2	.00	0	1100	391
17	16,000	7.0	.00	0	1100	391
18	16,000	6.9	.00	0	1500	391
19	16,000	7.0	10	8	540	394
20	16,000	No Sample	—	—	—	—
21	16,000	6.8	.00	0	1500	391
22	16,000	No Sample	—	—	—	—
23	16,000	"	—	—	—	—
24	16,000	6.2	30	24	240	192
25	16,000	6.2	30	24	360	287
26	16,000	7.0	10	8	150	120
27	16,000	6.7	.00	0	630	504
28	16,000	6.8	.00	0	660	528
29	16,000	7.2	10	8	540	432
30	16,000	7.0	10	8	360	288
31	16,000	6.1	.00	0	270	216
TOTAL	76,240					
AVERAGE		6.75	8.7	6.4	718	430

* samplers NOT operating (Maintenance problems)

cc. L.P. Hollabaugh
J. Wilkinfeld
T.A. Dunstedt
E.C.

FORM W2-52

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: 19 Mar 73

To : 303 Distribution

Re: 303-60

From : C. L. Parker

Subject: Plant Visit - Hooker Chemical Co.
Columbia, Tenn. 3/14/73

The Columbia, Tenn., plant of Hooker Chemical Company was visited on March 14 to collect data on waste effluent and waste abatement practices at their phosphorus and phosphoric acid plants.

Chief contact was Edward F. Smith, Sr., Manager, Environmental monitoring (located at Columbia).

Phosphorus

All the phosphorous for the Hooker Corporation is produced at Columbia. Ferrophosphorus is a collected by-product.

The phosphate ore is washed at a separate facility nearby. No water effluent is involved since local ore is merely washed and a mud pond formed. When the mud pond is filled it is abandoned and a new one started. The old one then dries. Both washed ore (sand) and unwashed ore are located into a nodulizer dryer and then the modules are fed into the furnace.

Heavy loads of fluorine gas are given off from the nodulizer. This is scrubbed with recycled lime slurry in large venturi contactors. The calcium fluoride formed is the major suspended solid.

Phosphorus particles from the furnace scrubbers are the other major suspended solid.

The Columbia plant waste system is a multiple pond arrangement operating as a closed loop. Water from the final pond is recycled to the supply pond. Phosphorus containing streams are sent to one pond series and fluoride wastes to another. Eventually they all come together and go through a lime slurry treatment station into a common system.

OKER CHEMICAL CORPORATION
LUMBIA, TENNESSEE

March 13, 1973

Plant Water System

The plant water system is based on a series of settling ponds. Lime is the only treatment used in the ponds and is added to the pond system after the initial (and major) settling has occurred. After the lime addition, other ponds settle the precipitate formed, and from the final pond the water is pumped to a supply pond.

The supply pond furnishes water for all uses that do not require city water. City water uses are for drinking and for sanitary use, for boiler feed, and for makeup to cooling towers. Most process and cooling water and some cooling tower makeup is supply pond water.

Effluent water from the processes and some cooling water, principally from the slag pits, is drained by three ditches to a collection sump. From this sump the water is pumped to the first of the settling ponds.

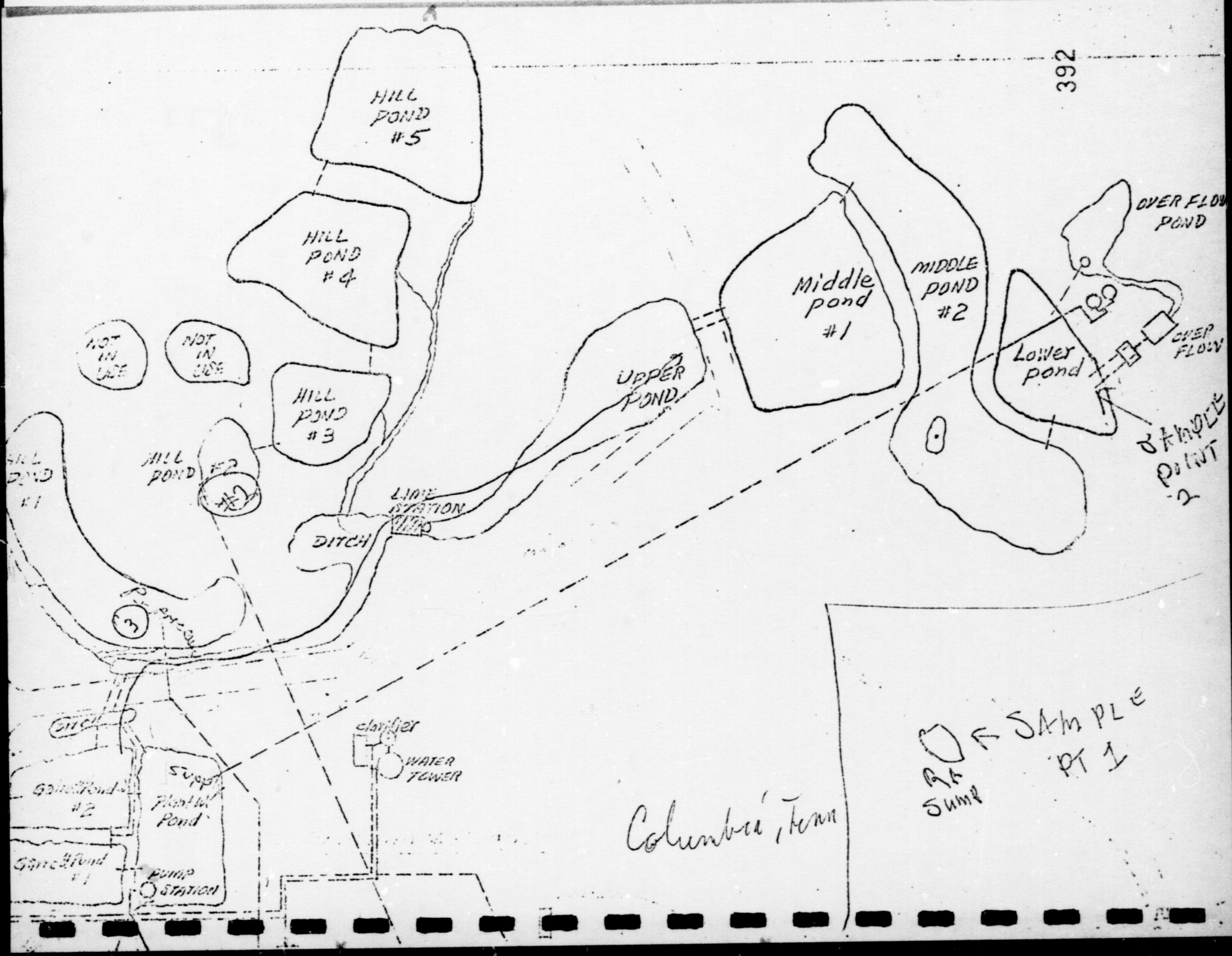
Phossy water (water which has contacted phosphorus) is collected in two other sumps and pumped to a separate group of settling ponds. The effluent from these ponds enters the main pond system near the point of lime addition.

There are three cooling tower systems in the plant: One supplies water to the large rotary kiln; a second supplies cooling water to the phosphorus furnaces; and a third supplies cooling water to the phosphoric acid plant and the small rotary kiln. There are varying amounts of tower system bleedoff or overflow which drain to the collection sump.

There are two small collection installations in addition to those previously mentioned. One collects and pumps drainage from a phosphate ore storage area to the main collection sump. The other collects water outside the final pond dike and pumps it into the final pond.

Any water makeup required for the plant water system is supplied from the river.

TTG/pr


HILL POND #5
HILL POND #4
NOT IN USE
NOT IN USE
HILL POND #3
HILL POND #2
#2
HILL POND #1
#3
DITCH
LIME STATION
UPPER POND
Middle pond #1
MIDDLE POND #2
Lower pond
OVER FLOW POND
OVER FLOW
SAMPLE POINT 2
DITCH
clarifier
WATER TOWER
Settling Pond #2
Settling Pond #1
Pump Station
Columbia, Tenn
SAMPLE PT 1
SUMP

ANALYSIS FORM

Plant HOOKER Date 4/1 Identifying No. C

Location COLUMBIA, TENN Sample Site PUGGY WATER POND

Product P_4, H_3PO_4

Parameter	Number of Measurements	Individual Measurements	Average
Flow	—	—	
Temperature	—	—	
Color	1	425 cobalt units (true color)	
Turbidity	1	370 FTU	
Conductivity	1	4100 mg/l NaCl / 8100 micromhos/cm	
Suspended Solids	1	380 mg/l	
pH	1	$6 < pH < 7$	
Acidity: Total	1	2800 mg/l as $CaCO_3$	
Free (M.O.)	1	-0-	
Alkalinity (Total) $\frac{P}{T}$			
Hardness: Total *	—	—	
Calcium	—	—	
Halogens: Chlorine			
Chloride	1	141 mg/l Cl^-	
Fluoride	1	550 mg/l	
Sulfate	1	26 mg/l	
Phosphates ~~(Total)~~ PO	1	1700 mg/l	
Nitrogen ~~(Total)~~ (NO)	1	11 mg/l as N	
Heavy Metals: Iron	1	14 mg/l	
Chromate	—	—	
Hydrogen Sulfide	—	—	
Oxygen (Dissolved)	—	—	
BOD	—	—	
COD	—	—	

REMARKS: * interferences with oxalate, indeterminate hardness.

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SIGNATURE(S) F. J. Bialas / Wesley Culbertson

ANALYSIS FORM

Plant HOOKER Date 4/2 Identifying No. B

Location COLUMBIA, TENN Sample Site R.R. Sump.

Product P_4, H_3PO_4

Parameter	Number of Measurements	Individual Measurements	Average
Flow			
Temperature	1	22.8°C	
Color	1	160 Apha Units (Intracolor)	
Turbidity	NT		
Conductivity	1	2100 mg/l Cl₂ ; 4400 μmhos/cm	
Suspended Solids	1	1650 mg/l	
pH	1	4.7	
Acidity: Total (pH 8.3 titration)	1	1050 mg/l as $CaCO_3$	
Free H_2O.	1	127 mg/l (as $CaCO_3$)	
Alkalinity (Total) P / T			
Hardness: Total	1	165 mg/l as $CaCO_3$	
Calcium	1	110 " "	
Halogens: Chlorine			
Chloride	1	130 mg/l	
Fluoride	1	270 mg/l	
Sulfate	1	390 mg/l	
Phosphates (Total)		700 "	
Nitrogen (Total) NO_3		16 " as N	
Heavy Metals: Iron	1	14 mg/l	
Chromate	—		
Hydrogen Sulfide	—		
Oxygen (Dissolved)	1	7.0 mg/l	
BOD			
COD	1	210 PPM	

REMARKS:

SIGNATURE(S) F.D. Bialas, Michael Callahan

ANALYSIS FORM

Plant HOOKER Date 9/2 Identifying No. A

Location COLUMBIA, TENN Sample Site RETURN POND

Product P_4, H_3PO_4

Parameter	Number of Measurements	Individual Measurements	Average
Flow			
Temperature	1	18.6°C	
Color	1	160 Apha units	
Turbidity	1	20 FTU	
Conductivity	1	1750 mg/l NaCl / 3290 μmhos/cm	
Suspended Solids	1	38 mg/l	
pH	1	6.0	
Acidity: Total (phen.)	1	1000 mg/l as $CaCO_3$	
Free (M.O.)	1	—0—	
Alkalinity (Total) P / M			
Hardness: Total	1	151 mg/l as $CaCO_3$	90 ?
Calcium	1	140 mg/l as $CaCO_3$	
Halogens: Chlorine			
Chloride	1	140 mg/l	
Fluoride	1	150 mg/l	
Sulfate	1	410 mg/l	
Phosphates (Total)	1	690 "	
Nitrogen (Total) NO	1	16 " as N	
Heavy Metals: Iron	1	6.0 mg/l	
Chromate		—	
Hydrogen Sulfide			
Oxygen (Dissolved)	1	9.4 mg/l	
BOD		—	
COD	1	190 ppm	

REMARKS: Data reported is at least 18 mos. old and not indicative of current situation (heavy rains & flooding recently, some said it was worst in 20 yrs.). Hooker plot sample analyses attached.

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SIGNATURE(S) T. A. Bialas, Michael Pelletier

HOOKER, COLUMBIA

(1) Plant Sewer – with plastic
(2) No. 6 – Tailings to plant outfall
(3) City Water
(4) RR sump – by Kiln area
Kiln Scrubber
(5) Back-Pond (100' from Upper end)
(6) Slag Sump (East End)
(7) [illegible]
(8) Cooling Tower?

Sample No →	1	2	3	4	5	6	7	8
Salinity	95	53	104	2.5	270	114	11	41
Hardness	3	2	1	13	11	4	11	4
COD	30	<20	<20	130	60	40	60	30
Total Solids	130	124	109	12,482	2,554	1,004	100	70
Total Dissolved Solids	130	94	105	12,482	2,312	1,004	100	70
Suspended Solids	0	30	4	0	242	0	0	0
Volatile	68	88	184	474	520	654	108	84
NH3 (as N)	0.10	0.13	<0.05	290	385	285	0.20	<0.05
N (KJ)	0.65	0.35	0.02	308	428	294	0.95	0.10
Nitrate (as N)	1.0	<1	1	4	8	3	1	<1
Total P	0.80	1.5	0.1	13	7	12	1.10	<0.1
Color	15	60	10	500	300	200	1,100	10
Specific Conductance (Moh)	220	140	260	4,600	1440	4000	250	270
~~total organic carbon (TOC)~~	6	4	5	60	17	14	5	3
~~Organic Nitrogen~~	0.55	0.20	0.20	175	42	14	0.75	0.10
~~Nitrite (as N)~~	<0.05	<0.05	<0.05	<0.05	1.4	2.4	0.05	<0.05
P as ortho	0.20	1.4	<0.1	7.0	4	8	0.40	<0.10
Sulfate (SO_4)	<5	13	26	1,100	900	1040	8	26
Sulfide ($S^{=}$)	<0.1	0.2	0.1	7.3	<0.1	<0.1	<0.1	<0.10
~~Sulfite (as SO3)~~ total chrom	<0.05	<0.05	<0.05	0.20	<0.05	<0.05	<0.05	<0.05
Cu	0.05	<0.05	<0.05	0.10	<0.05	0.05	<0.05	<0.05
Fe	1.0	1.0	<0.05	95	3.5	140	1.70	0.30
Pb	<0.01	<0.01	<0.01	1.1	0.28	0.20	0.01	<0.01
Manganese	0.10	0.09	<0.05	7.5	1.0	1.40	0.20	0.20
Hg	0.014	0.008	0.001	<0.001	<0.001	<0.001	0.004	0.005
Chloride	30	9	10	800	360	450	5	6
Fluoride	0.10	1.2	0.8	180	310	170	0.90	0.7
As	0.02	<0.02	<0.02	0.98	0.18	0.16	<0.02	<0.02
Cd	0.01	<0.01	0.01	0.6	0.01	0.05	0.01	<0.01
Zn	0.05	<0.05	0.05	1.4	1.2	0.70	<0.05	<0.05
Oil & grease	<1	<1	<1	<1	<1	1	<1	<1
Phenols	0.003	0.002	0.006	0.055	0.015	0.035	0.004	0.001
Hex-Chrom	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
PH	7.2	7.4	7.4	6.0	7.7	8.7	7.0	6.8

Remarks:
1 – Duck River
Cooling pump
2 – Old pond
overflow
3 – City water
4 – RR Sump
5 – Back pond (6)
6 – Slag Sump
7 – Back River
Williamsport
8 – Cooling tower

ANALYSIS FORM

Plant HOOKER Date 9/2 Identifying No. A

Location SUMMA, TENN Sample Site RETURN POND

Product P_4, H_3PO_4

Parameter	Number of Measurements	Individual Measurements	Average
Flow			
Temperature	1	18.6°C	
Color	1	160 Pt-Co units	
Turbidity	1	20 FTU	
Conductivity	1	1750 mg/l NaCl / 3250 μmhos/cm	
Suspended Solids	1	38 mg/l	
pH	1	6.0	
Acidity: Total (phen.)	1	1000 mg/l as $CaCO_3$	
Free (M.O.)	1	—0—	
Alkalinity (Total)			
Hardness: Total	1	191 mg/l as $CaCO_3$	90 n
Calcium	1	140 mg/l as $CaCO_3$	
Halogens: Chlorine			
Chloride	1	140 mg/l	
Fluoride	1	170 mg/l	
Sulfate	1	410 mg/l	
Phosphates (Total)	1	690	
Nitrogen (Total) NH	1	[illegible]	
Heavy Metals: Iron	1	6.0 mg/l	
Chromate	—	—	
Hydrogen Sulfide	—	—	
Oxygen (Dissolved)	1	9.4 mg/l	
BOD	—	—	
COD	1	190 ppm	

REMARKS: Data submitted in attachment is mislabeled and not indicative of current situation (heavy rains and flooding recently). Some data from most recent in-house lab. Hooker Plant sample analyses attached

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SIGNATURE(S) T. A. Bixler, Rachel Pollitzer

ANALYSIS FORM

Plant Hooker R Date 4/2 Identifying No. B

Location Columbia Div. Sample Site R.R Sump

Product P_4, H_3PO_4

Parameter	Number of Measurements	Individual Measurements	Average
Flow			
Temperature	1	22.2°C	
Color	1	160 apha Units (Hazen color)	
Turbidity	NT		
Conductivity	1	300 mg/l Mhos/cm ; 4000 µmhos/cm	
Suspended Solids	1	1600 mg/l	
pH	1	4.7	
Acidity: Total (Methyl Orange)	1	1050 mg/l as $CaCO_3$	
~~Free~~ M.O.	1	127 mg/l (as $CaCO_3$)	
Alkalinity (Total)			
Hardness: Total	1	165 mg/l as $CaCO_3$	
Calcium	1	110 " "	
Halogens: Chlorine			
Chloride	1	130 mg/l	
Fluoride	1	270 mg/l	
Sulfate	1	390 mg/l	
Phosphates (Total)		700 "	
Nitrogen (Total)		16 " as N	
Heavy Metals: Iron	1	14 mg/l	
Chromate			
Hydrogen Sulfide			
Oxygen (Dissolved)	1	7.0 mg/l	
BOD			
COD	1	210 mg/l	

REMARKS:

SIGNATURE(S) D. Beales, Michael P. Miller

ANALYSIS FORM

Plant HOOKER Date 4/3 Identifying No. C

Location COLUMBIA, TENN Sample Site DIESEL WATER POND

Product P_4, H_3PO_4

Parameter	Number of Measurements	Individual Measurements	Average
Flow	—	—	
Temperature	—	—	
Color	1	425 cobalt units (true color)	
Turbidity	1	370 FTU	
Conductivity	1	4100 mg/l as CaCO / 12100 micromhos/cm	
Suspended Solids	1	360 mg/l	
pH	1	6 < pH < 7	
Acidity: Total	1	7200 mg/l as $CaCO_3$	
Free (M.O.)	1	-0-	
Alkalinity (Total)	—	—	
Hardness: Total *	—	—	
Calcium	—	—	
Halogens: Chlorine			
Chloride	1	141 mg/l Cl^-	
Fluoride	1	950 mg/l	
Sulfate	1	26 mg/l	
Phosphates (~~Total~~)	1	1700 mg/l	
Nitrogen (~~Total~~) NO	1	11 mg/l as N	
Heavy Metals: Iron	1	14 mg/l	
Chromate	—	—	
Hydrogen Sulfide	—	—	
Oxygen (Dissolved)	—	—	
BOD	—	—	
COD	—	—	

REMARKS: * interferences with acidity, indeterminate by present method

SIGNATURE(S) D. H. Bivins / W. A. Chilton

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Hooker, Columbia split-sample analysis

	River H2O	RR dump	Return	Phossy Hse
pH	7.6	5.1	6.1	6.3
Hard	146	60	140 - 160	-
Ca Hard	130		20	-
Alk as CaCO3	N.L ← Alkalinity →	N.L	N.L	N.L
T.D.	113 ← tot (?) →	88	102	560
T.S.	.0	1,250	38	480
Tot Prof				
S.S.	145	2,100	2,225	4,800
D.O		7.8	8.5	
P. Prof	0.00	472	472	1026
P2O5	Tr.	472	824	1752

Mr C. Hall, Hooker lab personnel said that they performed alkalinity titration, but I can't figure out why.

PLANT WASTE ANALYSIS

COMPANY HOOKER CHEM CO.
PLANT LOCATION COLUMBIA, TENN
PRODUCT(S) PHOSPHORUS
IS THIS A STANDARD PROCESS FACILITY?

PLANT AGE JAN, 1953
TONS/DAY 45,000 P_2/YR
DATE 3/14/73
YES X NO

PROCESS FLOW DIAGRAM (SCHEMATIC)
(Please include location of waste streams)

ALL PHOSPHORUS CAPTIVE IN CORP. NONE SOLD ON OPEN MARKET. SMALL PART MADE INTO PHOSPHORIC ACID ON PREMISES.

RAW MATERIALS FOR PRODUCT

MATERIALS	ORIGIN AND PURITY COMMENTS
1. WASHED ORE (BENEFICIATED) - SAND	20% P2O5 PRIOR TO WASHING
2. UNWASHED ORE	(LOCAL ORE) 28% " AFTER "
3.	CA AND SILICA REMAINDER
4. COKE	~85% FIXED CARBON
5. SILICA	96% +SiO2
ENERGY - ELECTRODES	

STANDARD RAW WASTE LOADS

WASTE PRODUCTS	PROCESS SOURCE	LBS/TON OF PRODUCTS OPERATION AVE.	OPERATION RANGE	STARTUP AVE.	STARTUP RANGE	SHUTDOWN AVE.	SHUTDOWN RANGE
*1. FERRO PHOSPHORUS FURNACE		600 lb/TON					
**2. SLAG		10.8 TONS/TON					
***3. CO GAS		80,000 CFM/TON					
4. CaF + P2O4	SCRUBBING OF NODULIZER GAS	500 lb/TON					
5.							
6. IMPURE SILICA →	P. PROCESSING →						

FILTAID
ASBESTOS
ACTIVATED CARBON
COKE PARTICLES
PHOSPHATE PARTICLES

30 lb/TON — FILTERAID - 1.6 lb/TON
— ASBESTOS - 1.4
— CARBON - 2 lb/TON
PHOSPHATE
CORE PARTICLES } MIST & DUST

COMMENTS

* CLEAN UP AND SELL
** SELL FOR HIGHWAY USAGE & RAILROAD ROADBEDS
*** - USE AS FUEL
BURN IF NECESSARY

10.8 x 40,000 = 432,000

WATER INPUTS TO PLANT

TYPE	QUANTITY, GPD	COMMENTS ON SOLIDS, MINERALS, TREATMENTS, ETC.
RIVER	(EST) 115,000	SIMILAR TO RIVER WATER ANALYSIS ATTACHED
LAKE		
MUNICIPAL	430,000	ANALYSIS COPY ATTACHED
WELL		
~~OTHER~~ (RAIN)	244,000 (AVE)	

WATER USAGE

TYPE	TOTAL QUANTITY, GPD	% RECYCLED
COOLING (FURNACE SHELL + SLAG COOLING 7½%; ELECTRODES + (OTHER JACKETS) ~92½%)	9,650,000	90-95%
PROCESS (1) KILN SCRUBBER, 2) P CONDENSING, 3) P HANDLING)	11,720,000 TOTAL	80
OTHER → 75%		
OTHER → 21%		
→ 4%		

COMMENTS

RIVER WATER TAKEN IN AS NEEDED

* RECYCLED COOLING WATER HAS THREE TWO SYSTEMS - 1 - RIVER, 1 CITY, 1 POND MARSH.

WASTE TREATMENTS

STREAM NO. (Same as under previous Section)	TREATMENT METHOD(S)	FINAL STREAM DISPOSAL
1.	LIMING AT KILN SCRUBBER + PH TO 6.5 AT LIME STATION + SEDIMENTATION	TO LOWER POND + RECYCLE
2.		
3.	TO HILL PONDS TO ISOLATE P WASTE (SEDIMENTATION)	TO LIME STATION THEN TO UPPER POND
4.		
5.	SENT TO HILL POND #1, FOR SEDIMENTATION AND SLAG PERCULATION	TO LIME STATION AND UPPER POND

ANY SOLID WASTES ? YES

WHAT ARE THEY ? POND SOLIDS DREDGING

GARRETT - PERIODICALLY OTHERS LESS-FREQUENTLY

TREATMENT INVOLVED TO LAND FILL

QUANTITY, LB/TON OF PRODUCT WILL FORWARD.

PRESENT DISPOSTION

T. PONDS

EFFLUENTS FROM PROCESS AFTER ~~TREATMENT~~

STREAM NO.	SOURCE	GPD
1. (RECYCLING PROCESS AREA	1) SCRUBBERS & SPILLS	860,000
2. (FURNACE AREA	2) CONDENSING P + COOLING SHELLS & JACKETS	1,000,000
3.		
4.		
5. PHOSPHORUS PROCESSING AREA	3) FILTRATION, UNDERWATER STORAGE CENTRIFUGING	430,000

TO PONDS

COMPOSITION OF EFFLUENT STREAMS ~~AFTER TREATMENT~~

Constituents* Present	Stream	No. 1		No. 2		No. 3		No. 4		No. 5	
		AVE.	RANGE	AVE.	RANGE	AVE.	RANGE	AVE.	RANGE	AVE.	RANGE
	No. 1	(to SARRETT PONDS)									
Tot. Suspended Solids											
Tot. ~~Suspended~~ DISSOLVED Solids											
BOD											
COD											
pH											
Temperature											
Organics											
*											
*											
*											
*											

SEE ATTACHED SHEET

SEE ATTACHED SHEET

RAIL ROAD SUMP

BACK POND

*SEE ATTACHED LIST ON NEXT PAGE FOR ADDITIONAL APPLICABLE CONSTITUENTS AND TESTS. USE BACK OF THIS SHEET IF MORE ROOM IS NEEDED.

ADDITIONAL ANALYSES

TEST PARAMETERS

TURBIDITY
COLOR
CONDUCTIVITY
ACIDITY (FREE)
ACIDITY (TOTAL)
ALKALINITY (TOTAL)
HARDNESS (TOTAL)
HARDNESS (Ca)
HALOGENS: CL_2
Cl^-
F^-

SULFITE
SULFATE
PHOSPHATES: ORTHO
META
ELEMENTAL P
NITROGEN: NO_3^-
NO_2^-

HEAVY METALS: IRON
COPPER
CHROMATE
MANGANESE
VANADIUM
ARSENIC
MERCURY
LEAD

O_2 (Dissolved)

PRESENT TREATMENT INFORMATION

METHOD	WHEN INSTALLED	CAPITAL COSTS	OPERATING COSTS	STREAMS TREATED
1.	WILL FORWARD.			
2.				
3.				

PERFORMANCE OF TREATMENT METHODS

METHOD	QUALITATIVE RATING	WASTE REDUCTION* ACCOMPLISHED
1. CLOSED SYSTEM IN 1965		
2. WORKED SATISFACTORILY		
3. RAIN OVERFLOWS SOMETIMES OCCUR.		

*% REDUCTION IN WASTE LOAD AS MEASURED BY SUCH QUANTITIES AS TOTAL SUSPENDED OR DISSOLVED SOLIDS, CHLORIDES, SULFATES, pH, BOD, ORGANICS, ETC.

FUTURE TREATMENT PLANS

METHODS	ESTIMATED INSTALLATION TIME	ESTIMATED COST	ESTIMATED PERFORMANCE
1.	NONE		
2.			
3.			

GENERAL

1. DO YOU FORESEE ANY CHANGES IN YOUR WASTE LOAD IN THE NEXT FEW YEARS (RAW MATERIAL OR PROCESS CHANGES, PRODUCT PURITY, ETC.) ?

MAY HAVE MORE SCRUBBERS IN AIR POLLUTION CONTROL DEVICES. FURNACE SMOKE CONTROL

2. CAN THE PRESENT MANUFACTURING PROCESS BE MODIFIED OR CHANGED TO SIGNIFICANTLY REDUCE EFFLUENT WASTE LOADS ?

MAY HAVE MORE SCRUBBERS IN AIR AS ABOVE

CAN REDUCE BY EFFICIENT USE OF WATER.

3. DO "GOOD HOUSEKEEPING" PRACTICES HAVE A MAJOR BEARING ON YOUR EFFLUENT COMPOSITIONS OR ARE THEY COMPOSITIONS DETERMINED ENTIRELY BY BY-PRODUCTS OF THE PROCESS OR QUALITY OF RAW MATERIALS USED ?

NOT REALLY.

4. DOES THIS PLANT HAVE ANY UNIQUE WASTE SITUATIONS AS COMPARED TO OTHER PLANTS PRODUCING THE SAME CHEMICALS (RAW MATERIAL SUPPLY, PROCESS, GEOGRAPHICAL LOCATION, OTHER) ?

ORE PREPARATION MAY BE DIFFERENT FROM OTHERS, OTHERWISE PRODUCTS THE SAME
HAVE SUFFICIENT LAND FOR PONDING OPERATION
TVA USING CLARIFIERS
WORKING ON SLUDGE BURNING UNIT → SMALL UNIT NOW IN OPERATION

5. ARE THE TREATMENT PROCESSES NOW USED-----

a. SENSITIVE TO SHOCK LOADS?

HEAVY RAINS ONLY

b. SHUTDOWN AND STARTUP ?

c. MAINTENANCE REQUIREMENTS ?

PUMPING SENSITIVE

6. IS TECHNOLOGY AVAILABLE FOR ELIMINATION OF YOUR PLANT WASTE PROBLEMS ?

7. IF NOW AVAILABLE, WHAT DO YOU CONSIDER THESE TECHNOLOGIES TO BE ? (EVAPORATION, DISTILLATION, DEEP WELLS, AERATION PONDS, FILTRATION, NEUTRALIZATION, ETC.)

8. HOW DO YOU RATE THE COST OF UTILIZING THIS TECHNOLOGY IN SOLVING YOUR PLANT WASTE PROBLEMS ?

9. IF NOT AVAILABLE, WHAT TECHNOLOGY NEEDS TO BE DEVELOPED ?

10. IS ADDITIONAL RECYCLING OF EFFLUENT STREAMS PRACTICABLE ?

GONE ALL THE WAY NOW

11. ARE RECOVERY AND SOLID WASTE ISOLATION TECHNIQUES PRACTICABLE, AND IF SO, WHERE ?

LOOKING AT THIS NOW.

12. WILL THE INSTALLATION OF PROJECTED WASTE CONTROL FACILITIES CAUSE AIR, NOISE, THERMAL OR OTHER POLLUTION EFFECTS?

ARE INSTALLING ADDITIONAL AIR SCRUBBING. AIR SCRUBBER INSTALLATION MAYBE NOISY

13. ARE SPACE OR LAND REQUIREMENTS FACTORS IN FUTURE WASTE CONTROL PROJECTS ?

NO.

14. IF YOU WERE BUILDING A NEW PLANT COULD WASTE EFFLUENTS BE SIGNIFICANTLY REDUCED OR ELIMINATED ?

COMPLETE RECYCLE NOW; BELIEVE COULD IMPROVE IF STARTING OVER AGAIN.

15. MAY WE HAVE PERMISSION TO MAKE SPOT CHECK VERIFICATION MEASUREMENTS ON YOUR WASTE AND EFFLUENTS ?

YES.

16. IF SO PLEASE GIVE US:

NAME TO CONTACT ED SMITH - TED GARRETT

APPOINTMENT DATE(S) MARCH 29 - 30 WOULD LIKE TO DELAY UNTIL FOLLOWING WEEK

SAMPLE LOCATIONS (NEED PLANT LAYOUT WITH MARKED SAMPLING LOCATIONS)

NOTE: MARCH 26 WEEK IS SPRING VACATION. ED SMITH OTHERS OUT.

PLANT WASTE ANALYSIS

COMPANY HOOKER CHEMICAL CO. PLANT AGE 1959

PLANT LOCATION COLUMBIA, TENN TONS/DAY 130

PRODUCT(S) PHOSPHORIC ACID DATE 3/14/73

IS THIS A STANDARD PROCESS FACILITY? YES X NO ____

X EXCEPTIONS

PROCESS FLOW DIAGRAM (SCHEMATIC)

(Please include location of waste streams)

RAW MATERIALS FOR PRODUCT

MATERIALS	ORIGIN AND PURITY COMMENTS
1. PH	CAPTIVE
2. AIR	
3. H_2O	
4.	
5.	

STANDARD RAW WASTE LOADS

WASTE PRODUCTS	PROCESS SOURCE	LBS/TON OF PRODUCTS OPERATION AVE.	OPERATION RANGE	STARTUP AVE.	STARTUP RANGE	SHUTDOWN AVE.	SHUTDOWN RANGE
1. H_3PO_4	LEAKS & SPILLS	NO REAL MEASUREMENT					
2.							
3.							
4.							
5.							
6.							

NO ARSENIC - FOOD GRADE ACID ONLY TAKE OUT HERE GOES OUT IN ACID

99.9+ ACID RECOVERY - STACK TILT

COMMENTS

PANS ETC FOR LEAKAGE AT JEFFERSONVILLE AND TEXAS PLANT

NOTE: ARSENIC TREATMENT AT JEFFERSONVILLE TALK ABOUT

WATER INPUTS TO PLANT

TYPE	QUANTITY, GPD	COMMENTS ON SOLIDS, MINERALS, TREATMENTS, ETC.
RIVER		
LAKE		
MUNICIPAL	144,000 *	SAME AS P4 SHEET)
WELL	6,000 **	
OTHER	6,000 ***	

* MAKE UP TO TOWER

** WATER FOR ACID DILUTION + *** WATER FOR ACID

WATER USAGE

TYPE	TOTAL QUANTITY, GPD	% RECYCLED
COOLING	2,889,000	95 +%
PROCESS	12,000	NONE
OTHER		
OTHER		

COMMENTS

EFFLUENTS FROM PROCESS AFTER TREATMENT

STREAM NO.	SOURCE	GPD
1.	TOWER BLOWDOWN	72,000 GPD
2.	WASHDOWN FOR SPILLS ETC	15,000 GPD
3.		
4.		
5.		

COMPOSITION OF EFFLUENT STREAMS AFTER TREATMENT

Constituents* Present POR	Stream No. 1 AVE.	RANGE	No. 2 AVE.	RANGE	No. 3 AVE.	RANGE	No. 4 AVE.	RANGE	No. 5 AVE.	RANG
Tot. Suspended Solids										
Tot. ~~Suspended~~ DISSOLVED Solids	240									
BOD										
COD										
pH	6.6									
Temperature										
Organics										
POLY.	120 - LEAKAGE.									
*HARDNESS	132									
*PHENOL-PHTHALEIN ALKALINITY	NONE									
*METHYL ORANGE ALKALINITY	30									

*SEE ATTACHED LIST ON NEXT PAGE FOR ADDITIONAL APPLICABLE CONSTITUENTS AND TESTS. USE BACK OF THIS SHEET IF MORE ROOM IS NEEDED.

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NOTE! ED SMITH WANTS WANTS ANALYTICAL TESTS TO BE RUN AHEAD OF VISIT CALL HIM

ADDITIONAL ANALYSES

TEST PARAMETERS

TURBIDITY
COLOR
CONDUCTIVITY
ACIDITY (FREE)
ACIDITY (TOTAL)
ALKALINITY (TOTAL)
HARDNESS (TOTAL)
HARDNESS (Ca)
HALOGENS: CL_2
Cl^-
F^-
SULFITE
SULFATE
PHOSPHATES: ORTHO
META
ELEMENTAL P
NITROGEN: NO_3^-
NO_2^-

HEAVY METALS: IRON
COPPER
CHROMATE
MANGANESE
VANADIUM
ARSENIC
MERCURY
LEAD

O_2 (Dissolved)

WASTE TREATMENTS

STREAM NO. (Same as under previous Section)	TREATMENT METHOD(S)	FINAL STREAM DISPOSAL
1. BLOWDOWN	TO DITCH ONTO PONDS	
2. WASH DOWN	"	
3.		
4.		
5.		

ANY SOLID WASTES ? NONE

WHAT ARE THEY ? _____

TREATMENT INVOLVED _____

QUANTITY, LB/TON OF PRODUCT _____

PRESENT DISPOSTION _____

WASTE TREATMENTS

STREAM NO. (Same as under previous Section)	TREATMENT METHOD(S)	FINAL STREAM DISPOSAL
1.		
2. SAME AS POL P4		
3.		
4.		
5.		

ANY SOLID WASTES ? _____

WHAT ARE THEY ? _____

_____

TREATMENT INVOLVED _____

_____

QUANTITY, LB/TON OF PRODUCT _____

PRESENT DISPOSTION _____

_____

PRESENT TREATMENT INFORMATION

METHOD	WHEN INSTALLED	CAPITAL COSTS	OPERATING COSTS	STREAMS TREATED
1.	NONE			
2.				
3.				

PERFORMANCE OF TREATMENT METHODS

METHOD	QUALITATIVE RATING	WASTE REDUCTION* ACCOMPLISHED
1.		
2.		
3.		

*% REDUCTION IN WASTE LOAD AS MEASURED BY SUCH QUANTITIES AS TOTAL SUSPENDED OR DISSOLVED SOLIDS, CHLORIDES, SULFATES, pH, BOD, ORGANICS, ETC.

FUTURE TREATMENT PLANS

METHODS	ESTIMATED INSTALLATION TIME	ESTIMATED COST	ESTIMATED PERFORMANCE
1.			
2.			
3.			

HOOKER CHEMICALS & PLASTICS CORP., ET AL., Petitioners, v. RUSSELL E. TRAIN, Respondent.	No. 74-1683
HOOKER CHEMICALS & PLASTICS CORP., ET AL., Petitioners, v. RUSSELL E. TRAIN, Respondent.	No. 74-1687

CERTIFICATE OF SERVICE

I hereby certify that on this 20th day of December, 1974, one copy of the Deferred Joint Appendix to the briefs in the above-captioned cases was served on counsel for Respondent by placing same in the United States mail, first class, postage prepaid, properly addressed to John J. Zimmerman, Attorney, Department of Justice, Washington, D.C.

Henry J. Plog, Jr.

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December 20, 1974